SOIL ACIDITY, ALUMINIUM AND ADDED ORGANIC MATTER IN KRASNOZEM TOPSOILS IN RELATION TO PHOSPHORUS AVAILABILITY AND PLANT GROWTH

by

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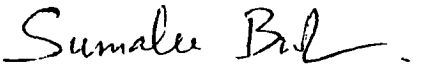

(S. Bunmongkolrat)

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

This thesis reports work on the effects of added, decomposable organic matter as a possible lime substitute on exchangeable and soil solution aluminium in relation to phosphorus availability and growth of perennial ryegrass (Lolium perenne. L) in acid krasnozems on Tertiary basalt, North-Western Tasmania. Soil was collected to a depth of 15 cm at three sites in a sequence of increasing elevation and rainfall, representative of the Burnie, Lapoinya and Yolla series.

The soil materials were first screened for their suitability for later work by determining certain basic soil properties and by measuring effects on these properties of glasshouse incubation for four weeks of soils with organic matter added as barley straw or lucerne chaff at rates equivalent to 0, 3.5 and 7.0 t/ha. There were significant effects, relative to initial levels of soil parameters, in terms of reduced exchangeable aluminium, increased available phosphorus and increased soil solution (pF2) ionic strength, with effects due to the addition of organic matter. Differences in cation exchange capacity sum of basic exchangeable cations, and soil reaction, were not significant.

Because it was highest in exchangeable aluminium, lowest in available phosphorus, and was strongly acid, Burnie soil material was used to study effects of different rates of added barley straw or lucerne chaff on soil aluminium, phosphorus, and soil solution ionic strength after different periods of incubation (0, 4, 8, 16 weeks), with and without added urea to bring the C/N ratio of the organic matter to a value of 12. The pH of the soils with added organic matter was higher than the controls, both with and without added urea, but the effect of urea on pH decreased with time. The effect of urea on the increase of pH was obvious in the first 4 weeks and then slightly varied from week 4 to week 8. Thereafter, the pH was on the decline. Exchangeable aluminium was lower in soil incubated with organic matter but differences due to rate of added organic matter were not significant, lucerne chaff had a greater early effect but the difference versus barley straw was reduced after four weeks. There was a sharp rise in available phosphorus measured after four weeks in

all soils with added organic matter but this was followed by a rapid fall so that levels at the end of the experiment (16 weeks) were well below those at its commencement. Available phosphorus of control soils decreased regularly throughout. There was little difference in effects due to kind of organic matter. Ionic strength of soil solution extracts (pF2) from the soils with added organic matter rose sharply and levels were maintained in soils with added organic matter.

Burnie soil was again used to follow effects of added organic matter on active aluminium in relation to native available phosphorus and growth of "Nui" cultivar of perennial ryegrass. Urea was not added in this experiment. Soluble aluminium was added as $Al_2(SO_4)_3.14H_2O$ after four weeks of incubation of soil plus organic matter (Sequence (a)) and together with organic matter (Sequence (b)), both sequences being incubated for a further four weeks before sowing of ryegrass seed. Differences between the two sequences in effects on pH, soil solution phosphorus (pF2), phosphorus uptake and dry matter production by the test plant were not significant. However, there were marked effects within each sequence of added organic matter in increasing values of each of these parameters in relation to controls. Exchangeable and soil solution aluminium, especially monomeric aluminium, were markedly reduced by added organic matter at all rates of aluminium application and these effects were greater in Sequence (a) than in Sequence (b) soils. Aluminium remaining in solution was almost wholly in organic complexed forms. Conversely, available phosphorus was higher. Lucerne chaff was slightly but consistently more effective than barley straw but these differences were not significant.

Finally, Lapoinya soil from the "museum" area of Elliott Research Station was used in a study of effects of both added organic matter and phosphorus (KH_2PO_4) on soil aluminium in relation to growth of ryegrass because of its low pH, very low level of available phosphorus and high level of active aluminium. Reduction of exchangeable and monomeric aluminium occurred with rate of phosphorus application, the effect being greater in the presence of added organic matter. Again,

nearly all of the soil solution aluminium was in organically complexed forms in the presence of added organic matter. Differences between the effects of lucerne chaff and barley straw were small but consistent, although not statistically significant, with lucerne chaff having the greater effects. Soil reaction again increased with added organic matter and an inverse relationship between levels of aluminium (both exchangeable, monomeric form) and available phosphorus depended on pH. Plant growth and phosphorus uptake and content responded by increasing sharply with rate of phosphorus application and were further enhanced greatly by added organic matter. Plant symptoms of aluminium toxicity/phosphorus deficiency were not evident in the presence of added organic matter, even at the highest level of aluminium application (100 ppm, O.D.).

Both forms of organic matter used whether fresh or partly decomposed, gave beneficial effects within the period of experimentation in suppressing aluminium toxicity and enhancing growth of perennial ryegrass in the acid soils used. Application of organic matter at practical rates may allow reduction of the quantity and frequency of lime additions.

1. LITERATURE REVIEW

1.1. Acidification of Agricultural Soils

Soil acidity is an important factor limiting plant growth in many parts of the world (Pearson, 1975; McLean, 1976; Kamprath, 1978; Adams, 1978, 1981). It can be caused not only by natural processes of acidification but also by man's industrial and agricultural activities. The latter are much more important in accelerated soil acidification.

1.1.1. The process of soil acidification

Soil acidification occurs when acids or acid-producing substances are added directly to, or produced within, an agricultural ecosystem. Direct additions include materials such as fertilizers containing sulphur and/or nitrogen and gaseous or finely particulate constituents such as sulphur dioxide and ammonia falling as "acid rain". These substances may undergo hydrolysis, oxidation or nitrification in soil with the production of hydrogen ions. Common examples are the nitrification of ammonium and the oxidation of sulphur, viz.,

(i) Nitrification of ammonium

$$2NH_4^+ + 3O_2 \quad \_\_\_\_ \quad 2NO_2^- + 2H_2O + 4H^+$$

(ii) Oxidation of elemental sulphur

$$2S + 3O_2 + 2H_2O \quad \_\_\_\_ \quad 2SO_4^= + 4H^+$$

Acids can be produced within a natural or agricultural ecosystem during the soil nitrogen, carbon and sulphur cycles (Gillman, 1987). More than one mechanism of acidification may operate at any one time. In natural ecosystems, soil acidification is a continuous and long term process that is activated when water percolates through the soil profile . But it has recently become a matter of serious concern in Australia that this process can be accelerated by agricultural practices (Nyatsanga and Pierre, 1973; Helyar, 1976).

The rate of soil acidity increase varies with many factors. These include the addition of acidifying fertilizers, rate of addition and turnover of organic matter, and the removal of agricultural products without fertilizer compensation (Williams,

1980). Generally, the rate of acidification is greatest in light-textured soils of low initial organic matter content.

1.1.2. Factors affecting soil acidification

Soil nitrogen: A comprehensive review of the nitrogen cycle in relation to soil acidity has been reported by Helyar (1976). An estimate of the net acidity appearing in an agricultural ecosystem can be made from a consideration of differences in form and quantity of nitrogen gain and loss. Losses of nitrogen may occur when product is removed and/or nitrate is leached. Helyar (1976) concluded that the addition of nitrogen as ammonium fertilizer and its loss as nitrate induced soil acidification unless the base accompanying nitrate was replaced.

These effects have been demonstrated in many recent studies (Jarvis and Robson, 1983(a); 1983(b)). In pot experiments with a poorly buffered and acidic sandy soil from an area of elevated lateritic sandplain in the wheatbelt of Western Australia at Bodallin and Badgingarra, nitrogen (N) was supplied to plants either as nitrate (NO_3^-), ammonium (NH_4^+) or through symbiotic fixation. Soil acidity decreased or was little changed when plants took up nitrate but increased by over 1.0 pH unit when plants took up ammonium and by up to 0.6 pH unit when nitrogen was fixed by legumes. Also, Mason (1980) showed that wheat yields in field and pot trials were reduced when nitrogen was supplied as ammonium sulphate at the rate of 376 kg/ha (76 kgN/ha) for a number of years. He noted that long-term use of ammonium sulphate was associated with reduced soil pH, lower levels of exchangeable cations such as Ca, Mg, and K; and markedly increased exchange acidity measured as exchangeable H^+ and active Al and Mn. It was considered that Al toxicity was the direct cause of reduced yield of wheat.

Soil organic matter: Soil organic matter can release organic acids which are mostly weak acids containing carboxylic, phenolic and amino-nitrogen groups. Thus the soil becomes acid because of soil organic matter accumulation but it cannot become strongly acid by this mechanism due to buffer effects (Allison, 1973; and Stevenson, 1982)

In Australia, leguminous pastures have long been used to improve soil fertility with accompanying increased organic matter and acidity levels in surface soils. For example, Williams (1980) showed that on yellow podzolic soils of the Southern Tablelands of N.S.W., the establishment and maintenance of legume pasture for 50 years had increased surface soil acidity by nearly 1 pH unit. However a higher organic matter content can induce not only increasing soil acidity but also increasing cation exchange capacity (CEC) and titratable acidity.

More recently it has been recognized that the decline of soil pH can extend into the subsoil below the organic-matter-rich surface layer. Helyar (1976) has suggested that this may be due to another important factor i.e., depletion of the more basic exchangeable cations associated with increased leaching of nitrate following the input of legume nitrogen and progressive dominance of the exchange complex by aluminium.

Not all pasture soils will develop metal toxicity problems with increasing acidity. The outcome depends upon various soil properties, in particular the chemical nature and quantities of Al and Mn in soils, and whether decreasing pH induces a critical level of soluble Al and/or Mn for plant toxicity (Williams, 1980). For example, the critical level for Al toxicity to barley was 0.55 me 100 g^{-1} or 11 % Al saturation of the effective CEC in Tatum silt loam soil at the Virginia Agricultural Experiment Station (Adams and Pearson, 1967). In a red-yellow podzolic soil 0.2 me 100 g^{-1} or 4 % of the total soil Al were critical for alfalfa (Moschler et al., 1960).

A number of workers have shown that exchangeable aluminium can be reduced in the presence of organic matter (Jackson, 1963; Pearson, 1975; Sanchez, 1976; Thomas and Hargrove, 1984). The aluminium complexed by organic matter is rather stable. This aluminium is not exchangeable with molar potassium chloride and obviously not easily titratable (Bloom et al., 1979; Hargrove and Thomas, 1981a; 1982a). In fact, organic matter may contribute very little to the effective CEC of some acid soils if they contain appreciable quantities of aluminium, so strongly is the aluminium associated with soil organic matter (Posner, 1966; and Sanchez, 1976).

Removal of agricultural products: Generally, plants absorb more cations or positively charged nutrients such as ammonium (NH_4^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) than anions or negatively charged nutrients such as nitrate (NO_3^-), phosphate ($H_2PO_4^-$, HPO_4^{2-}), sulphate (SO_4^{2-}) and chloride (Cl^-). To maintain internal ionic charge balance within the plant cell plants produce organic acids, retain the organic anions within their tissue and excrete hydrogen ions (H^+) into the soil (Raven and Smith, 1976). There is no effect on soil acidity if these hydrogen ions are consumed in the process of decomposition following return of all the plant materials to the soil. However, if some or all of the plant materials are removed eg., directly as hay and grain and indirectly as animal products, the excreted H^+ ions remaining in the soil can cause soil acidity. Also, the depletion of basic cation reserves in the soil can induce soil acidity because of increasing dominance of acidic cations on the soil exchange complex (Gillman, 1987).

There are various factors promoting soil acidification by crop removal. These include the type of plant and the form of nitrogen taken up (Jarvis and Robson, 1983 a,b). These workers showed that wheat and perennial ryegrass were less alkaline than subterranean clover and white clover so that removal of the legumes resulted in more acidification than removal of the cereal and grass. Also considerable changes in the acidity of the soil of the rhizosphere can be due to differences in cation/anion balance in plants supplied with different forms of nitrogen (Smiley, 1974; Soon and Miller, 1977; Nye, 1981). Acidification is greater where ammonium-N is the main form absorbed by plants and least where nitrate-N is absorbed. The uptake of nitrate sometimes may lead to decreased soil acidity or increased soil pH if plants (e.g. gramineous plants) absorb excess anion (ie. NO_3^-) and excrete alkali (OH^-) into the soil (Israel and Jackson, 1978).

Direct effects from polluted environments: The deposition of acids or acid formers from polluted air in rainfall, "acid rain", in heavily industrialised regions and downwind from them has caused noticeable effects in decreasing soil pH and increasing aluminium dominance of soils (Friesen et al., 1980). In some soils with

high levels of heavy metals such as Zn, Cu, Pb, Ni and Cd, increasing soil acidity has given rise to active levels of these elements that are toxic for plant growth. Mine wastes may be an important local source of stream and soil pollution by such heavy metals (Cassel, 1980; Grove et al., 1981; Pavan et al., 1984).

1.1.3. Effects of soil acidification on plant growth

Low pH in acidic soils rarely causes direct effects in reduced plant growth. However in some legumes relying on nitrogen fixation, low soil pH has a direct effect on nodulation. This is because Rhizobium spp. are more sensitive to low soil pH than the host legume (Andrew, 1976). For instance, in strongly acid soils in North East Victoria, the growth of soil Rhizobium is limited when soil pH_W (pH measured in a slurry of 1 part soil and 5 parts water) is below 5.5. This affects the nodulation of subterranean clover, and then reduces the growth of the clover (Coventry et al., 1984).

As soil pH declines chemical reactions occur which result in: (i) increasing solubility of soil aluminium and manganese to levels toxic to plant growth and (ii) decreasing concentrations of soluble phosphorus, calcium, magnesium and molybdenum to levels that may be inadequate for the growth of plants (Jackson, 1967; Foy et al., 1978). These indirect effects of soil pH in reducing plant growth depend on both soil type and plant species or cultivar. Aluminium toxicity is not usually found in sands or in the absence of aluminosilicate clay even at a pH_W of 4.5, nor in organic soils. Furthermore, recent work in South-West N.S.W. has shown that different soils (red earths and red-brown earths) on the same parent rock (parna) appear to be acidifying at different rates under similar management (J.A. Beattie, personal comm.). However, in many krasnozem soils in Tasmania, aluminium toxicity of sensitive plant species may occur at a pH_W of about 5.0 (Temple-Smith, personal comm.). Plant species and varieties may differ widely in tolerance to excess aluminium in the growth medium (Foy, 1974). Also in the same plant genotype, the problem of aluminium toxicity may be different even at similar soil pH (Foy et al., 1978). These differences should be genetically controlled (Reid, 1971).

Because of the complexity of relationships between soil pH, type and amount of clay-size soil particles, levels of exchangeable cations, kind and content of organic matter, and the plant factors, it may be difficult to identify the specific reason(s) for poor plant growth on acidic soils. Nevertheless, Al and Mn toxicities are the main limiting factors to plant growth in most acid soils. In soil where active aluminium is present at high levels, deficiencies of essential elements such as P and Ca may occur. Aluminium forms highly insoluble compounds with P and if aluminium dominates the exchange complex, Ca may be too low..

Aluminium toxicity symptoms include abnormal root growth. The whole root system becomes " coral shaped " with many stubby lateral roots lacking fine branches. Under these conditions, the ability of the root system to take up water and nutrients is much reduced (Foy et al., 1978).

In subsoils with high aluminium levels, tap root growth is poor and may be limited to the surface soil where acidity is lower. Under these conditions, most of the roots grow horizontally (Temple-Smith et al., 1983).

Al toxicity to leaves is normally not as severe as to roots. Jackson (1967) reported that leaf colour often turns to dark green but occasionally a purplish colour develops in either leaves or stem bases. Sometimes, yellowing and chlorosis occurs resulting in drying of the leaf especially from the tip and margins.

In some cases Ca deficiency symptoms caused by excess aluminium may be due to reduced mobility of Ca in plants. The symptoms in this case are normally specific to young leaves. In severe cases the young leaves curl and roll and eventually the growing point is entirely destroyed (Foy et al., 1978).

Mn toxicity does not appear to affect root growth but causes chlorosis and necrosis of the margins of older leaves (Foy et al., 1978).

1.1.4. Amelioration of soil acidity

Liming is still the conventional method for amelioration of soil acidity and to restore fertility. It is well known that liming improves soil conditions for better growth of plants by first increasing soil pH (Bhaumik and Asthana, 1969; Evans and

Kamprath, 1970; Kamprath, 1978; Cassel, 1980; Thomas and Hargrove, 1984) which has its effects on decreasing concentration of exchangeable aluminium and improved nutrient availability (Evans and Kamprath, 1970; Pearson, 1975; Farina et al., 1980). In fact, lime may not be a plant growth factor per se, its effect being first to neutralize soluble aluminium in the soil and then enhance the concentration of soluble phosphorus for the crop (Kunishi, 1982).

Amarasiri and Olsen (1973) found that lime did not increase soluble phosphorus and labile phosphorus in an acidic oxisol from Colombia, South America, until the pH_{CaCl2} was approximately 6.5. They suggested that the limed soil had a greater adsorption capacity for phosphorus compared with unlimed soil because of phosphorus adsorption by freshly precipitated aquo-hydroxy compounds of iron and aluminium at the pH of the limed soil.

Overliming can have negative effects in decreasing plant growth (Shoop et al., 1961; Reeve and Sumner, 1970). These authors suggested that overliming may detrimentally affect the availability of micronutrients as the pH becomes more alkaline. For example, the solubility of Fe and Mn falls sharply above pH_W 6 ; B, Cu and Zn above pH_W 7 ; P and K above pH_W 7.5 ; and N above pH_W 8. Only S, Ca, Mg and Mo show little change above pH_W 8.5, with S and Mo remaining unaffected to pH_W 10. Generally, liming to pH_W 7 is a common practice in many temperate regions (Munns, 1965; Mc Lean, 1976; Kamprath, 1978; Farina et al., 1980) and this would seem to be a reasonable compromise to achieve a relatively long-lasting effect in relation to continuing acidification. In some soils with insufficient Mg, liming may decrease the level of exchangeable Mg below a critical level for crops (Lund, 1970; Grove et al., 1981; Pavan et al., 1984).

1.1.5. Soil acidification in Tasmania

Acidity of soils in Tasmania is the result of long-continued leaching, the nature of the parent rock and soil age. In North-Western Tasmania, krasnozem soils have developed from basalt (Stephens, 1937; Stephens et al., 1942). These soils are more acid as the rainfall increases with increasing elevation and distance from the

coast. They have a moderately acid surface horizon near the coast (pH_W about 5.8), but this changes to strongly acid inland (pH_W about 5.3) (Loveday and Farquhar, 1958).

Acid soils in Tasmania utilized for long-term pasture are mainly light sands high in organic matter. Some short-term pasture is included in rotations on heavy-textured krasnozems frequently used for intensive cropping, especially potato (Paton, 1963). However, it is very difficult to estimate the actual rate of acidification of any Tasmanian pasture soils due to the common use of lime at the time when the pasture species were established (Paton, 1960). Thus, there is no strong evidence so far to confirm or deny that there is a soil acidity problem in Tasmanian pasture soils. Nevertheless Tasmanian authorities are now participating in an Australia-wide investigation of soil acidification consequent upon the introduction of legume-based pastures in rotations which became general some 30 years ago.

Recently acidification has been recognized in soils subject to regular application of nitrogenous fertilizer for intensive fruit cropping e.g. berry fruit plantations in Southern Tasmanian. The soils in question are clay loams and loams overlying acid clay subsoils (Murray-Prior and Temple-Smith, 1981; Temple-Smith, 1984). The effect of application of sulphate of ammonia to horticultural soils of the Murrumbidgee Irrigation Areas, New South Wales, was reported many years ago (Groenewegen and Bouma,1960). In some cases soil reaction had fallen to pH_W 4.3, virtually the ultimate pH for these soils and highly favourable for aluminium toxicity.

1.2. The Role of Organic Matter in Soil Fertility

1.2.1. Introduction

The terms "soil organic matter" and "humus" have been used interchangeably and in practice include all the organic materials and compounds in the soil including soil microbiomass (living microbial tissue) but excluding macroflora and macrofauna (Stevenson, 1982). The formation of humus depends upon the rate of decomposition and synthesizing processes which are governed by many factors

(Allison, 1973). In general, humus or soil organic matter, can be divided into two main groups designated as non-humic and humic substances.

The non-humic group includes uncoloured and low-molecular-weight compounds which can be utilized as substrates by soil microorganisms and may have a transient existence in the soil, eg., amino acids, aliphatic and aromatic acids, carbohydrates, hydrocarbons, alcohols, auxins and aldehydes. The humic substances comprise yellow to brown or black coloured, high molecular weight polyphenolic complexes which are synthesized in and distinctive to the soil. They are also, as distinct from non-humified organic matter, relatively stable (Kononova, 1966), even in agricultural soils under exploitive uses, although other forms of soil management have actually resulted in maintenance of original levels or production of higher levels of soil organic matter.

Humic matter may be divided into three broad classes according to the classical, empirical method of extraction :

(a) Fulvic acid (soluble in acids and alkalis)

(b) Humic acid (insoluble in acids but soluble in alkalis)

(c) Humin (insoluble in both acids and alkalis)

(Kononova, 1961; Stevenson, 1982). No sharp distinctions can be made between these fractions which appear to be merely segments of very large molecular complexes with a wide range of molecular weights. However qualitative or even semi-quantitative distinctions have been made by certain authors, particularly the Russian workers. The dynamics of soil organic matter which play a major role in natural ecosystems and extensive agriculture have been reviewed by Paul (1984) and Tiessen et al. (1984).

In mainland Australia most arable surface soils have low organic matter contents (average less than 1.5 %) because of low rainfall and or high temperature (Davidson, 1986). In Tasmania normal levels of soil organic matter are much higher ranging from 3-4 % up to 8-12 % in mineral soils (CSIRO Division of Soils, unpublished data). Exploitive agricultural practices have led to severe reduction of soil

organic matter content of many soils with accompanying degradation in both physical and chemical properties (Davidson, 1986).

1.2.2. Organic matter and soil fertility

Soil organic matter can influence soil fertility both directly and indirectlly. Soil organic matter has long been recognized as a reservoir of plant nutrients and a major factor contributing to favourable soil physical, chemical and biological properties (Kononova, 1961; Allison, 1973; Stevenson, 1982; Vaughan and Ord, 1985). Appropriate management of this resource should make it possible to increase the efficiency of utilizing both soil and fertilizer nutrients, particularly in areas where the cost of fertilizer is high (Davidson, 1986).

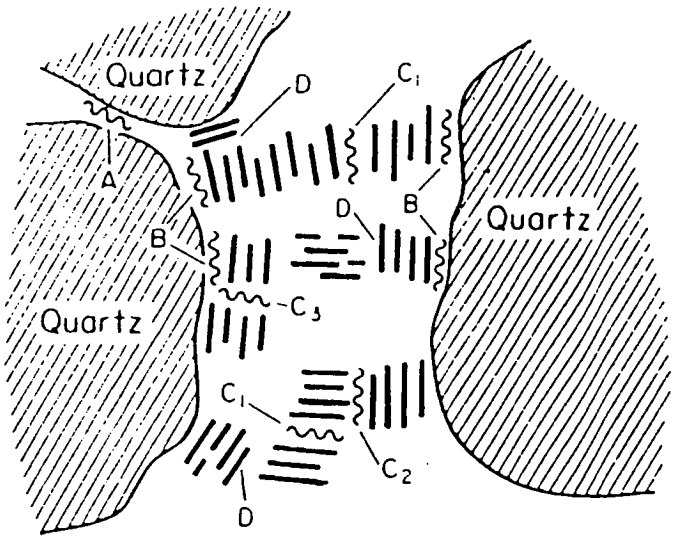
Direct effects on plant growth: The roles of simple organic compounds such as aliphatic and aromatic acids, vitamins and auxins have been comprehensively discussed including their stimulatory and/or inhibitory effects on plant development (Hartley and Whitehead, 1985; Lynch, 1985). Under certain conditions during the decomposition of plant materials, the amounts of some organic substances may rise to phytotoxic levels e.g. phenolic compounds, consisting of vanillin, syringaldehyde, ferulic, syringic, vanillic and p-hydroxybenzoic acids (Börnor, 1960; Toussoun et al., 1968; Patrick, 1971; Lynch, 1976). The effect of these chemicals on plant growth has been termed "allelopathic" and a number of reviewers have described allelopathic effects e.g., Rice (1974), (1979); Putnam and Duke (1978). Moreover, some volatile fatty acids (VFA' s) e.g., acetic acid and butyric acid can be released and accumulated to reach phytotoxic levels under anaerobic conditions (Lynch, 1977). For example, acetic acid around 4 to 5 mM and butyric acid at about 0.5 mM, at pH 6.0 to 6.3, can inhibit the growth of wheat seedlings (Wallace and Elliot, 1979). The type of VFA' s produced depends upon time, temperature and pH of organic residue decomposition (Playne, 1978). Recently, Hicks (1989) has studied the effects of VFA' s in soil with incorporated straw on barley growth under a range of temperature conditions in the glasshouse. He reported that higher

concentrations of acetic acid than of butyric acid occurred at the higher temperature (17-25 °C) while at lower temperature (5-15 °C) acetic acid concentrations were lower than those of butyric acid. In the early stages of decomposition under anaerobic conditions, phytotoxic materials may be produced in considerable quantity (Patrick, 1971). However, under aerobic conditions production of these substances stops rapidly and microbial materials are synthesized.

Indirect effects on plant growth: Soil organic matter influences soil physical, chemical and biological properties.

Humus assists the process of soil aggregation and is a major factor in maintaining soil structure and stability (Rose, 1966). A model to illustrate the possible mechanism of micro-aggregate formation in soils has been proposed by Emerson (1959), and is shown in Figure 1.1. Many serious problems arise with degradation of soil structure. These include a lack of large soil pores for drainage and aeration in clay soils, reduced water holding capacity in sandy soils, increased susceptibility to compaction and soil erosion (Tisdall et al., 1978; Pera et al., 1983).

The buffering effect of organic matter can prevent rapid changes of soil pH (Allison, 1973; Stevenson, 1982; Davidson, 1986). Colloidal humic substances may account for a wide range of soil cation exchange capacity while the CEC of isolated fractions of humus may vary from 300 to 1400 me $100g^{-1}$ (Stevenson, 1982). Colloidal complexes of humic substances and clay usually have a net negative surface charge. The surface density of charge is variable but that of humus is usually much higher than for clay minerals. Various cations are held with different strengths in relation to type of colloid, exchange capacity, and valence and hydrated radius of cations (Bohn et al., 1979). For these reasons, soil cation exchange capacity (CEC) is strongly affected by organic matter which plays a far more important role than its relatively small percentage content in mineral soils would indicate (Kamprath and Welch, 1962). In fact, it is found that from 20 to 70% of CEC may be contributed by soil organic matter depending on soil type, including mineral composition and amount and type of organic matter (Stevenson, 1982). This role of humus is more important in



Types of bond:

A. Quartz-organic matter-quartz.

B. Quartz-organic matter-domain.

C. Domain-organic matter-domain.

C1, face-face

C2, edge-face

C3, edge-edge

D. Domain-domain, edge-face.

Figure 1.1 Possible arrangements of clay domains, organic matter, and quartz in a soil crumb (after Emerson, 1959).

sandy soils than in clay soils. Simpson (1983) reported that the CEC of well-decomposed humus may exceed 300 me $100g^{-1}$ humus compared with only 80-150 me $100g^{-1}$ for montmorillonite, 30-40 me $100g^{-1}$ for illite and 3-15 me $100g^{-1}$ for kaolinite. However the high buffering capacity of acid organic soils may be a disadvantage in economic terms because much more lime may be needed to bring the pH to a desired level.

Soil temperature is an important controlling factor of soil biological activity and for plant growth especially in the temperate regions. The dark brown colour of humic substances means that more heat energy can be absorbed during the day while more back radiation occurs at night. This can be advantageous for a warmer surface soil in daytime while frost hazard may be reduced by nocturnal back radiation (Swift et al., 1979).

Soil organic matter acts as a reservoir of plant nutrients and as an energy substrate for microorganisms. It is also effective in reducing leaching losses of soil nutrients (Allison, 1973; Simpson, 1983). Nevertheless, nutrient elements in soil organic matter are usually present in forms that are unavailable for immediate plant uptake and do not become available until they are converted by microorganisms to available forms such as NH_4^+ or NO_3^-, $H_2PO_4^-$ or HPO_4^{2-} and SO_4^{2-} (i.e. they are "mineralized"). The amounts of elements such as N, P and S that are released by mineralization vary with many factors, including soil properties, vegetation, management practices, and climate (Kowalenko, 1978). In general, organic N is the dominant form of N in most surface soils accounting for more than 95 % of total soil N (Allison, 1973).

The amounts of available forms of soil N present are due to the net effects of two biological processes, i.e. mineralization and immobilization, which may occur concurrently but with opposite effects (Anderson and Vaughan, 1985). This has led to use of the term "Mineralization Immobilization Turnover" (MIT) (Campbell, 1978). The net result of MIT, which depends also on the C/N ratio of organic residues undergoing decomposition, determines the availability of soil N. Since the fraction of

organic N in soil is rather stable but by no means inert, it can be considered as a short to medium term resource of N for plant growth.

Organic sulphur is the major component of S in most surface soils. The situation of phosphorus is variable. Organic P may vary from as little as 3% to as much as 75% of the P in surface soils with inorganic P varying from 97% to 25%. Thus in many soils of low organic content (i.e. most Australian soils) inorganic P is a major component of the total soil P. Most inorganic forms of phosphorus are unavailable to plant growth due to their very low solubility. Soluble phosphorus reacts with aluminium, iron and manganese in acid soils and with calcium in alkaline soils to form insoluble phosphates and there is also the possibility of adsorption of phosphorus by clay minerals and secondary carbonates (Stevenson, 1982). However, a number of workers have shown that addition of organic matter to soil can enhance phosphate availability (Whitehead, 1963; Chater and Mattingly, 1979; Jenkinson and Ladd, 1981). This influence of organic matter on soil phosphate availability will be discussed in more detail below (section 4).

Soil organic matter can form stable complexes with some metals, particularly heavy metals, and affect their availability to plants and soil microbes (Stevenson, 1982). This effect is most important in acid soils where aluminium and iron may otherwise be toxic to plants. The effectiveness of humic substances to complex or chelate with metals depends upon the nature, position and number of functional groups such as carboxyl, acid-hydroxyl, phenolic-, alcoholic-, and enolic-hydroxyl (Linehan, 1985). The effects of such complexing, including chelation, will be discussed below (section 3).

Soil organic matter may adsorb and degrade pesticides via the biological activities of soil microorganisms. Normally the pesticide molecules are broken down to simple inorganic compounds e.g. CO_2, H_2O, NH_3, PO_4, H_2S, SO_4, Cl, Br, As, Hg and others (Bollag et al., 1968; Crosby and Li, 1969; Martin, 1972). The presence of these breakdown products in soil may or may not be important in causing detrimental effects on plant growth. To illustrate this point, inorganic bromide accumulating in soil

after fumigation with ethyl dibromide or methyl bromide may account for growth inhibition or injury to carnation, beans and cabbage seedlings (Brown et al., 1958; Stelmach, 1958). Such phonomena have both advantages and disadvantages from an agricultural point of view. Soil organic matter can detoxify and degrade certain pest control substances which are harmful to animal health e.g. 2,4-dichlorophenoxyacetic acid and other organic herbicides, including phenylcarbamate, phenylurea, and chlorinated aliphatic acid herbicides (Alexander, 1965; Kearney et al., 1965; Kearney and Kaufman, 1969; Loos, 1969). On the other hand, such substances have to be applied to the soil in greater quantities in relation to the level of organic matter to obtain desired control effects.

It is well known that different kinds of decomposition products have different abilities to retain herbicides. Dunigan and McIntosh (1971) studied natural soil organic matter and noted that humic acids and lignins were highly effective absorbers of atrazine, protein was of intermediate effectiveness, polysaccharide-type components had low effectiveness, while ether- and alcohol- extractable constituents of soil organic matter (such as waxes, fats and resins) had no capacity to adsorb atrazine. Moreover Hayes et al. (1968) found that humic acids retained s-triazine more effectively than fulvic acids. Reviews of the interaction of organic matter with pesticides, fungicides, and herbicides in soil have been presented by Khan (1978) and Stevenson (1982).

1.2.3. Processes of decomposition

Many studies of the decomposition of different plant materials in different soils under different conditions have been reported (e.g. Dickinson and Pugh, 1974; Swift et al., 1979). Rates of decomposition depend upon the activities of numerous and varied soil microfauna and microflora populations. Bacteria and fungi play the major role. However, some soil animals such as earthworms are also very important in the incorporation of plant residues into the soil, especially in the initial mixing process (Allison, 1973).

The decomposition process and its rate in the short term have been recorded simply by periodic measurements of the weight loss of organic residue. More precise long-term studies of decomposition processes have been made possible by the introduction of techniques using isotopically-labelled plant materials (Stevenson, 1982) The process of decomposition of organic matter in relation to mineralization/immobilization of phosphorus in soil will be reviewed briefly.

Breakdown of organic residues: The numbers and types of soil microorganisms which take part in the decomposition process depend upon the quantity, type, and accessibility of organic matter. The organic residues are basically made up of polysaccharides, lignins, proteins and fats with smaller quantities of simple sugars, aliphatic acids and phenols, and larger amounts of other substances (Bernfield, 1963). When soil environmental conditions are favourable, organic residues can be degraded rapidly by soil microbes.

Upon addition of organic residues into soil the decomposition process begins with their breakdown to simple organic compounds involving extracellular enzymes of heterotrophs. Other organisms oxidize these compounds to smaller units by means of intercellular enzymes. Finally, a wide range of organic compounds is excreted by soil microbes while some elements are immobilized in microbial tissues (Alexander, 1961). Although the initial chemical nature of organic residues may be variable, the metabolic sequences within the microbial cell follow similar pathways (Allison, 1973).

The different organic components of plants and animals are decomposed at different rates because the proportions of their resistant constituents are different (Parsons and Tinsley, 1975; Martin and Haider, 1977; Sorensen, 1977; Martin and Haider, 1979). For example, lignins, other phenolic substances and waxes from plants are either slowly decomposed or are rather stable in soils. Humic polymers existing in soil seem to be stable with a slow rate of degradation of 2-5 % per annum depending upon environmental conditions (Haider, et al., 1974). On the other hand some highly degradable organic substances such as sugars, proteins, amino acids, aliphatic acids

and many polysaccharides may release about 80 to 90 % of their C in a few hours or days (Martin and focht, 1977).

The role of decomposer organisms: The decomposer organisms play a very important role in accelerating the rate of decomposition. They can be classed into two major groups i.e. microflora (e.g. bacteria, actinomycetes, fungi and yeast) and micro- and macro-fauna (e.g. nematodes, protozoa, earthworms and microarthropods) (Swift et al., 1979). Further details of the roles of these organisms have been discussed by Dickinson and Pugh (1974) and Swift et al. (1979). A brief discussion will be presented here.

In most environments, fungi are the first decomposers followed by bacteria (Lynch, 1976). Cole et al. (1978) showed that bacteria could rapidly immobilise labile inorganic soil P while carbon substrates were being metabolised, but most of the bacterial P was subsequently mineralized to inorganic P by amoebae. The efficiencies of inorganic P uptake from soil by microorganisms and plant roots have been compared and it has been shown that soil microbes, particularly bacteria, have very efficient P-uptake mechanisms (Beever and Burns, 1976). Cole et al. (1977) found that decomposers took up phosphorus 3 to 5 times faster than plant roots in a simulation model for P-cycling in semi-arid grasslands. The uptake, storage and utilisation of P by fungi have also been discussed by Beever and Burns (1981). The population of active decomposers is found mostly in the rhizosphere rather than dispersed in the bulk soil (Greaves and Webley, 1965). Nematodes have been found to enhance organic-P mineralisation by shortening the decomposition cycles (Anderson et al., 1982). Moreover, earthworm activity is important in P turnover in low-P soils by increasing decomposition rates (Mansell et al., 1981).

1.2.4. Factors affecting decomposition

As the decomposition of organic materials is the result of complex interactions between microbial activity and size of populations, it is affected by many factors including environment, quality of substrate, and other soil factors.

Environmental factors: Two main factors will be emphasized.

(a) Temperature This is a major factor affecting organic matter decomposition. Different decomposers have different temperature optima for their growth (Alexander, 1977). At higher temperatures CO_2-loss and the rate of tissue breakdown are greater than at lower temperatures e.g. Pal et al. (1975) showed that decomposition of plant residues such as rice straw increased with temperature between 7 and 37°C. The combined effect of high temperature and moisture is more important than that of temperature alone because it favours microbial growth and increased decomposition rate (Jenkinson and Ayanaba, 1977).

Wide temperature fluctuations in the surface soil adversely affect microbial growth, multiplication, and other activities. Biederbeck and Campbell (1971) reported that sub-zero temperature had only a slight effect on viability of soil microorganisms. Thawing after freezing appeared to be highly lethal to microflora. This apparently affects mineralization and immobilization of P (Saunders and Metson, 1971; Dalal, 1977). The mineralization of P in crop residues can be as effective as added fertilizer P in terms of availability to crops if the temperature is above 20 °C and available moisture is adequate (Abbott, 1978). At temperatures below 20 °C, however, immobilisation of the major plant nutrients by soil microorganisms such as yeasts, fungi and actinomycetes is favoured. In this respect yeasts play a dominant role in the soil (Cheshire et al., 1976).

(b) Moisture content In general, organic residues are decomposed at maximum rate over a wide range of moisture contents (Jenkinson, 1981). The metabolic processes of decomposition and synthesis are slow in poorly drained soils under anaerobic conditions because of lack of oxygen.

It has been noted that the effect of moisture on release of P from plant material added to soil is variable (Blair and Boland, 1978). On the other hand, in dry soil, the release of appreciable amounts of both inorganic P and organic P from dead microbial cells, plant tissues and autolysed plant materials has been widely reported (Newberg, 1979; Brookes et al., 1982; Jones and Bromfield, 1982). When soil is

rewetted following desiccation, available P from cell debris and root tissues rapidly re-enters the P-cycle to be utilised by microbes and plants, or adsorbed by soil colloids.

Quality of substrate: The rate of decomposition varies widely with the substrate quality of decomposing materials. Generally, the types of organic residues can be used as a criterion to predict the rate of litter degradation. To illustrate this point, the decomposition of plant residues containing large quantities of nitrogen with a low C:N ratio is rapid while decomposition of residues high in lignin and polyphenol is obviously retarded.

It is well known that nitrogen content of plant materials is an important factor controlling their decomposition rate (Aber and Melillo, 1980). A number of workers have shown that the application of nitrogen to litter materials or incorporated crop residues can increase their decomposition rate (Mahendrappa, 1978). The C:N ratio has an effect on the release of nitrogen from decomposing materials. It is a useful index to determine whether the quantity of soil nitrogen is adequate for plant growth through the processes of immobilization and mineralization or not. If soil organic materials with a high C:N ratio (>25 to 30:1) are incorporated into cultivated soils, net nitrogen immobilization is usually expected to occur (Allison, 1973). When crop residues of low C:N ratio are incorporated with soil, net nitrogen mineralization can be observed enhancing the rate of residue decomposition.

Lignin is an important source of structural units for humus (Martin et al., 1980). These workers studied humus formation by using ^{14}C-labelled organic substrates and found that most of the lignin carbons were incorporated into highly resistant or aromatic fractions of soil humus.

Many workers have demonstrated that the initial lignin content of the litter plays a more important role in controlling the rate of decomposition than does nitrogen (Berg and Staaf, 1980; Melillo, et al., 1982). Also, more nitrogen will be retained during decomposition if the initial lignin content is high (Melillo et al., 1982).

Polyphenolic compounds in plant materials are widely recognised as modifiers of the rate of decomposition (Swift, et al., 1979), and it has been noticed

that the rate of litter decomposition and nitrogen release is obviously reduced in the presence of high levels of polyphenols.

Retardation of decomposition by polyphenols is believed to be associated with the inhibition of soil fungal activity. Harrison (1971) reported that the high polyphenolic content of oak and beech leaves was able to suppress the growth of many fungi. The amount of polyphenols in the leaves can also be directly regulated by plants in response to the amount of nitrogen available in soil. Davies et al. (1964) revealed that plants will normally synthesize large amounts of polyphenolic compounds in foliage when the soil supply of nitrogen is low so that the rate of litter decompositiion is reduced.

Soil factors: Some important soil factors affecting decomposition rate are soil reaction (pH), inorganic nutrients, and clay content.

(a) Soil reaction is one of the most important factors influencing decomposition of organic residues. Decomposition usually occurs faster in neutral than in acid soils. Soil acidity can reduce not only the activities of soil organisms but also the size of their populations. Generally, soil organic phosphorus appears to be much less stable in neutral or alkaline than in acid soils because the activities of soil microorganisms decrease with increase of soil acidity (Enwezor, 1967).

Quin and Rickard (1983) reported that the addition of lime to a New Zealand pasture soil under irrigation raised the pH_W from 5.8 to 6.5 with the release of inorganic P as a result of enhanced microbial activity. However they also found that this mineralized P may not be immediately available to plants because of its accumulation as insoluble Ca-bound P which may then be solubilized gradually as the pH declined again.

Soil pH may not be a good index for mineralisation of organic P because the pH of the rhizosphere and that at the root surface may differ by as much as 1 to 2 pH units from the pH of the adjacent bulk soil (Nye, 1981). Hedley et al. (1982) explained that in a low P soil, a drop of approximately 2 pH units due to the release of

H^+ from plant roots was responsible for solubilization of non-exchangeable inorganic P and increasing availability of P to plants.

(b) Inorganic nutrients Soil microorganisms need many necessary nutrients for their activities as do higher plants. These nutrients, especially N, P, K, Ca, Mg and S, must be supplied from the available soil nutrient pool or from decomposing organic materials. In the former case especially, microorganisms may offer short-term competition to higher plants for the available nutrient supply. Among these nutrients competition for nitrogen may be the most intense and nitrogen starvation of young crops sown too early after incorporation of organic residues of high C/N ratio is a well-known phenomenon. Immobilization of P has often been found during decomposition such as in the litter layer of forest soils (Ausmus et al., 1976), in grass residues, especially in old pasture (Floate, 1970 b), and in soil after incorporation of wheat straw (Brown and Dickey, 1970). Generally, light-textured soils have considerably lower levels of organic P than clay soils (Kaila, 1963).

Imbalance of nutrient elements in soils may limit the activity of soil microbes. For example, in P-deficient soils the rate of N mineralization may be decreased but after application of phosphate fertilizer the rate of mineralization may be enhanced (Munevar and Wallum, 1977). The addition of salts or fertilizers to soils can cause both net N and P immobilization, mineralization or have no effect (Dalal, 1977; Batten et al., 1979; Hedley et al., 1982). However, high salt concentrations may be toxic to the soil microbial population (Alexander, 1977).

(c) Clay content It is well known that increasing soil organic matter content and/or decreasing decomposition rate is directly related to increasing clay content (Appiah and Thomas, 1982). Clay has long been known to be responsible for stabilizing humus and/or retarding its degradation (Mattson, 1932). Clay minerals may form stable complexes with both organic compounds and humic substances that are resistant to both biodegradation and high temperature (Greenland, 1971; Stevenson, 1982). Organic substrates may be sorbed on either external or internal clay surfaces and in the latter case especially the organic matter may be difficult of access for

microbial attack (Theng, 1974; Burns, 1978). The rate of decomposition has been found to decline in proportion to the surface area of clay minerals (Zunino et al., 1982). Thus biodegradation is retarded more in the presence of montmorillonitic (2:1 type) clays than kaolinitic clays. The association of clay with newly synthesized materials, extracellular metabolites, or extracellular enzymes of microorganisms has also been observed to retard decomposition rates of these substances (Burns, 1978).

Edwards and Bremner (1967) proposed that the binding mechanism(s) between humic substances and clay minerals involved linkage of electrically neutral clay mineral and organic matter particles by cations such as Al^{3+}, Fe^{2+}, Mn^{2+}, Ca^{2+} on exchange sites to form soil microaggregates of less than approximately 250 μm size. Larger aggregates could be formed through "polymerization" of these microaggregates. Furthermore, Mortland (1970) suggested that the functional groups of organic matter could be linked to polyvalent cations through a water bridge. A number of workers have extensively reviewed these mechanisms (Greenland, 1971; Theng, 1979; Burchill et al., 1981). Soils of variable charge such as krasnozems and andosols, containing large amounts of amorphous aluminosilicates, accumulate large quantities of very stable organic matter having strong organo-clay mineral bonding (Tate and Theng, 1980; Zunino et al., 1982).

1.3. The Effect of Organic Matter on Aluminium Toxicity in Acid Soils

Organic matter is considered as an ameliorant of harmful effects of active aluminium on plant growth in addition to its well-documented benefits for other physical and chemical properties of acid soils. The mechanism(s) of suppression of aluminium activity by soil organic matter are still being investigated actively (G.S.P. Richie personal comm.)

1.3.1. Aluminium toxicity in soils

Aluminium is a major component of most mineral soils. Its principal forms of occurrence are as a structural ion in aluminosilicate clays, in polymeric aquohydroxy sesquioxide complexes, and in resistant forms such as gibbsite and certain heavy minerals. During the weathering process and particularly as a result of

breakdown of clay minerals, aluminium is released into the soil solution where it may undergo a series of hydrolytic reactions, resulting in increased soil acidity (Jackson, 1963). A comprehensive review of the considerable literature on the chemistry of aluminium in soils is beyond the scope of this study and discussion will be restricted to consideration of aluminium toxicity to plant growth.

Aluminium toxicity has long been recognized as one of the major factors limiting plant growth in acid soils (Foy, 1974; McLean, 1976; Alam and Adams, 1979; Carvalho et al., 1980; Adams and Moore, 1983; Thomas and Hargrove, 1984; Kim et al.,1987). Soluble aluminium has been known to be well correlated with plant growth since the early 1950's (Khasawneh, 1971; Adams, 1974; Sparks, 1984), but the critical concentration of aluminium for toxicity effects varies among soils (Adams and Lund, 1966; Evans and Kamprath, 1970). It is clear that the intensity of aluminium toxicity is highly correlated with the activity of monomeric aluminium in the soil solution (Adams and Lund, 1966; Pavan et al., 1982). Generally, aluminium may be present in the soil solution in both monomeric and polymeric forms but only monomeric aluminium ions are phytotoxic and their activities are considerably influenced by the ionic strength of the soil solution and pH (Alva et al., 1986a; and Blamey et al., 1983). Alva et al. (1986 b) found that the best index for aluminium toxicity was the sum of the activities of the monomeric species (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3^{o}$, and $Al(SO_4)^{+}$). However, this parameter would be a good predictor of aluminium toxicity for a given plant species only if (i) the ratio of the amount of aluminium taken up by the plant and the content of the element in the soil solution is low enough that the solution activity does not change substantially with plant uptake or if (ii) any change in aluminium activity due to plant uptake is readily buffered by release of aluminium from the solid phase or other soluble but non-toxic forms, such as polymeric or organic forms (Alva et al., 1986(b); Kim et al., 1987). If these conditions are not met for a given soil, a combination of activity and an estimate of buffer capacity to maintain aluminium activity in the soil solution, correlated with

plant performance, may offer the best prediction value (Edwards, D.G. personal comm.).

Widely proposed as useful diagnostic aids are pH (Adams and Lund, 1966; Evans and Kamprath, 1970; Carvalho et al., 1980), exchangeable aluminium (Pearson, 1975; Sanchez, 1976; Kamprath, 1978, 1984), degree of aluminium saturation of exchange complex (Kamprath, 1978; Adams and Moore, 1983; Kamprath, 1984), and level of aluminium in solution (Adams and Lund, 1966; Pavan et al., 1982; Adams and Moore, 1983; Adams and Hathcock, 1984;). Evans and Kamprath (1970) reported that most of the poor plant growth in acid soils occurred when the pH_{KCl} was below 5.0, or pH_{KCl} 5.5 in kaolinitic soils (McCart and Kamprath, 1965). The critical soil pH at which aluminium may reach toxic levels depends upon a number of factors which include type of clay mineral, concentrations of cations, anions and total salts, soil buffering capacity, organic matter content, and plant species (Foy, 1974).

The amount of aluminium, generally presented as "exchangeable aluminium", extracted by unbuffered neutral 1 M KCl solution has been used extensively in soil acidity investigations, particularly for estimating lime requirement (Kamprath, 1984). Pearson (1975), Sanchez (1976) and Kamprath (1978) showed that improvement in plant growth after liming a given soil was well correlated with reduction of the amount of exchangeable aluminium. Much poorer correlations were obtained when comparisons were made across a wide range of soils (Adams and Lund, 1966, and Adams and Hathcock, 1984). Thus, while the degree of aluminium saturation has been shown to be a useful parameter for prediction of aluminium toxicity (Kamprath, 1984), the critical percentage saturation may vary widely amongst different soils for the same plant species so that the relationship between aluminium saturation and aluminium toxicity is not consistent (Adams and Moore, 1983).

Adams and Moore (1983) and Adams and Hathcock (1984) found that there is no consistent relationship between concentration and activity of aluminium in the soil solution on the one hand and aluminium toxicity to cotton roots on the other.

Their results indicated that some soluble aluminium ions may chelate with organic compounds producing anions which are not phytotoxic. However earlier analytical methods may not distinguish between toxic and such non-toxic forms of aluminium in solution.

Recently Kerven and Edwards (1987) have described a method capable of discrimination between inorganic monomeric and organically complexed forms of aluminium in soil solution extracts involving a short-term colorimetric reaction. Use of this method may lead to better understanding of many effects of soil acidity on plant growth and the behaviour of nutrient or toxic substances in acid soils.

In conjunction with such data, plant symptoms can be interpreted for more precise diagnosis of aluminium toxicity even when they are not clearly defined. Details of these symptoms have been reviewed by Foy (1974, 1984).

1.3.2. Effects of organic matter on aluminium in soils

The nature and role of soil organic matter in soil fertility and its reactions with soil aluminium have been reviewed by Kononova (1966), Stevenson and Ardakani (1972) and Linehan (1985). A number of investigations have shown that soil organic matter is capable of forming complexes or chelates with metals such as aluminium and that such complexes are important in plant nutrition (Bremner et al., 1946; Himes and Barber, 1957; Evans and Kamprath, 1970; Bartlett and Riego, 1972; Hoyt and Turner, 1975; Ahmad and Tan, 1986). Brogan (1964), Hoyt and Turner (1975), and Thomas (1975) found that the levels of soluble and exchangeable aluminium ions were reduced by adding organic matter to very acid soils. Also it has been noted that soils high in organic matter often contain only small quantities of soluble aluminium (Evans and Kamprath, 1970). Recently it has been reported that decomposed plant materials seem unlikely to contribute to soil acidification if they have high concentrations of anions, and that their effects on soil pH may be widely different in relation to both type of soil and kind of agricultural practices (Ritchie and Dolling, 1985). Organic residues may be as effective as lime in reducing aluminium phytotoxicity (Ahmad and Tan, 1986).

Soil organic compounds that form stable complexes with metal ions (e.g. AL^{3+}, Fe^{2+}, Mn^{2+}) can be divided into two main groups:

(a) Non-humic substances or biochemical compounds which still retain their own physical and chemical characteristics and have chelating characteristics; these include amino acids, polyphenols, carbohydrates, proteins, polysaccharides and low-molecular-weight organic acids. Most of these compounds are continuously produced in soil through the activities of microorganisms but persist for only a short time before conversion.

(b) Humic substances or complex polymers formed by secondary synthesis reactions and produced during the advanced stages of decomposition of organic residues. They appear to be aromatic, hydrophilic, chemically complex, polyelectrolyte-like materials that have a wide range of molecular weights varying from a few hundred to many thousands. They are also acidic and dark coloured. These humic substances are commonly divided into three main fractions (Kononova, 1966; Stevenson, 1982) as follows :

(i) Humic acid which is precipitated on acidification of the alkaline extract but is soluble in dilute alkali.

(ii) Fulvic acid which is soluble in both dilute acid and dilute alkali and remains in solution when the alkaline extract is acidified.

(iii) Humin which is not extracted from the soil by dilute acid or dilute alkali.

These three fractions are similar in structure but are distinctive in molecular weight and number of functional groups. For example, fulvic acid has a lower molecular weight but contains more oxygen-containing functional groups (e.g., carboxyls, hydroxyls and carbonyls) per unit weight than the other two fractions (Schnitzer and Khan, 1972).

The first group of transient metabolic compounds appears in appreciable quantities in the rhizosphere or near decomposing plant residues where microbial activity is intense. The soluble or mobile forms of metals such as Al and Fe in soils are

mainly complexed with these biochemical molecules while the second group (or humic substances) forms insoluble metal-organic complexes (Stevenson and Ardakani, 1972).

Generally, in soil amended with organic wastes or manures the biochemical compounds should be relatively active in chelating with metals. However, these chelation complexes may be of little importance in soil because they are rapidly broken down by microorganisms. Thus the most significant complexes of this type in soils are those involving high-molecular weight humic substances (humic and fulvic acids).

The ability of humic acids and fulvic acids to form stable complexes with aluminium depends upon the number of oxygen-containing functional groups, e.g., carboxyl , phenolic hydroxyl, and amide groups (Schnitzer, 1978). Some workers have shown that the proximity of -COOH and -OH groups in humic and/or fulvic acids is important in relation to their capacities for complexing aluminium (Schnitzer, 1969; Motekaitis and Martell, 1984). The stability of aluminium complexed with relatively low molecular weight fractions appeared to increase inversely with distance between adjacent carboxylic groups within the molecule or directly with increase of basicity. On the other hand, the formation of aluminium complexes with polymeric carboxylic acids of high molecular weight may be due partly to the inherent ability of the carboxyl group to bind aluminium and/or partly to strong binding with particular arrangements of ligands or with the increase of basicity in the polymer (Shigemitsu and Kumada, 1981). If the molecular weight of the organic matter is known, the weight ratios of the combination between metals and organic matter can be expressed as molar ratios. For Al^{3+} and Fe^{3+} complexes, water insolubility increased over a range of molar ratios from 1:1 to 6:1 (Schnitzer and Skinner, 1963).

The possible mechanisms of the reaction between organic matter and aluminium ions involving complexing or chelation, complex coagulation, and peptization reactions have been defined by Stevenson (1982) as follows:

(a) Chelation occurs when two or more coordinate positions about the metal ion are replaced by donor groups of a single ligand to form an internal ring structure; stability is increased when the link between metal and chelant involves more than one bond.

(b) Coagulation is the precipitation of colloids by means of enzymes or chemical agents to form a jelly-like, soft mass. In soil, humic and fulvic acid, like other organic colloids, can be precipitated from solution by electrolytes, the intensity of flocculation varying with factors such as pH and the nature of electrolytes.

(c) Peptization is a process of dispersion of insoluble particles by mechanical means to form a colloidal solution. Many research workers have discussed these mechanisms and their interaction in detail e.g., Mortensen (1963), Bartlett and Riego (1972), Ca brera and Talibudeen (1977), and Stevenson (1982).

Humic acids persist in acid surface soils mainly because of their resistance to decomposition. A number of workers have shown that soluble aluminium can be detoxified by adding humic acids, with the formation of organo-aluminium complexes through the mechanisms mentioned above (Brogan, 1964; Schnitzer and Khan, 1972; Tan, 1978)

Recently, Tan and Binger (1986) found that added humic acid suppressed reduction of leaf phosphorus concentration. This may be due to humic acid chelating with aluminium, rendering aluminium inactive for reaction with phosphorus in the soil solution, allowing greater availability of phosphorus for plant growth.

In acid subsoils of the Coastal Plain, Southeastern United States, root proliferation is generally limited by aluminium toxicity (Adams and Hathcock, 1984). Pavan et al.(1982) discovered that level of toxicity was positively correlated with Al^{3+} activity in Ultisols and Oxisols from Southern Brazil. However toxicity could be reduced in the presence of organic matter and depended upon the kinds and concentrations of organic acids present in the soil solution. Hue et al. (1986) analysed soil solutions from many eluviated acid subsoil horizons of Ultisols on the Coastal Plains of Alabama and found that a number of organic acids occurred at higher

concentrations in forested areas than in cultivated soils. Bruckert (1970a) reported that citric and oxalic acids were strong complexers of aluminium while malic and malonic acids were moderate and lactic and succinic acids were weak complexers.

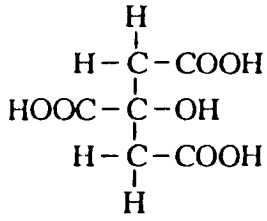
Furthermore, the effectiveness of organic acids in reducing aluminium toxicity also may be associated with the position of carboxyl and hydroxyl groups on their main carbon chain (Hue et al., 1986). It is obvious that the most effective detoxifying organic acids have either two carboxyl groups directly connected (e.g., oxalic) or two pairs of carboxyl and hydroxyl groups bound to two adjacent carbons (e.g., citric and tartaric). The moderately detoxifying group of acids has either a pair of carboxyl and hydroxyl groups similarly attached (e.g., malic and salicylic) or two carboxyls attached to a common carbon atom (e.g., malonic). The last group of weak aluminium detoxifiers comprises those acids that do not possess the structural configurations mentioned above, with the exception of lactic acid (see Figure 1.2)

In the soil solution the effectiveness of organic acids in inhibiting the hydrolysis of aluminium is variable and also depends on concentration. Kwong, Ng Kee and Huang (1979) showed that the stability constants of organic complexes with aluminium varied in the order citric acid > malic acid > tannic acid > aspartic acid > p-hydroxybenzoic acid.

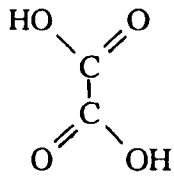
1.4. The Interaction of Organic Matter and Phosphorus in Acid Soils

In acidic soils, the fate of added phosphate depends on soil factors such as pH, exchangeable aluminium, active aluminium and iron oxides, clay content and organic matter (Larsen, 1967; Lopez-Hernandez and Burnham, 1974; Parfitt, 1978; White, 1980). Sesquioxidic aquo-hydroxy aluminium and iron complexes are considered to provide the main sites for phosphate adsorption in acid to near neutral soils (Hingston et al., 1967; 1969). Phosphate is sorbed on active surfaces via anion adsorption and precipitation processes. Such phosphate sorption tends to be reduced if inorganic anions (Barrow, 1974) and organic anions (Deb and Datta, 1967; Nagarajah et al., 1968; 1970) can compete with phosphate for sorption sites.

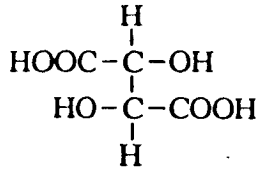
The most effective detoxifying acids.



Citric

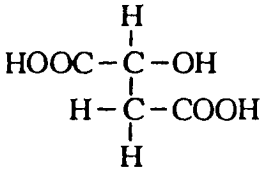


Oxalic

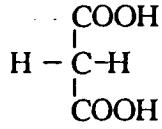


Tartaric

The moderately effective detoxifying acids.



Malic



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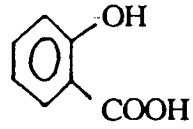
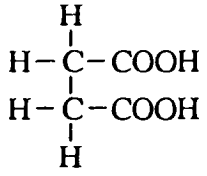
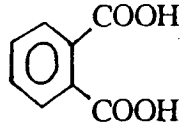


Salicylic

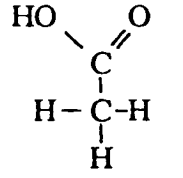
The least effective detoxifying acids.



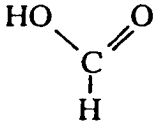
Succinic



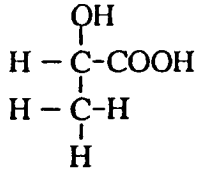
Phthalic



Acetic



Formic



Lactic

Figure 1.2 Configurations of some organic acids. (after Hue et al., 1986)

The effects of organic anions on phosphate sorption have been recognized increasingly over the past 35 years (Swenson et al., 1949; Deb and Datta, 1967; Nagarajah et al., 1968; Nagarajah et al., 1970; Earl et al., 1979; Lopez-Hernandez et al., 1979; White, 1981; and Haynes, 1982). There appear to be three possible mechanisms:

(i) competitive sorption reactions involving metal-phosphate or metal-organic ligand bonding in the formation of precipitates or surface complexes (Nagarajah et al., 1968; Lopez-Hernandez et al., 1979),

(ii) the dissolution of phosphate adsorbents by organic ligands (Earl et al., 1979) which refers to the role of organic acids in chemical weathering (Stevenson, 1982),

(iii) the modification of the surface charge of phosphate adsorbents by organic ligand sorption (Nagarajah et al., 1968; Kwong and Huang, 1979) involving an indirect effect of organic ligand sorption on phosphate retention.

These three types of reaction of organic anions and phosphate in acid soils are much affected by pH, P-concentration, and the form of the organic anions. White (1981) and Haynes and Ludecke (1981) studied the effect of pH on phosphate adsorption and reported that in acidic soils in which hydrated Al and Fe oxides were dominant, phosphate solubility may either decrease with increase of pH (above 4) or show no marked change. Haynes (1982) pointed out that the chemical basis of this observation could be the hydrolysis of exchangeable aluminium and the subsequent reaction of the newly formed surface hydrolytic species with phosphate from the soil solution. The optimum pH range for maximum adsorption of phosphate by aluminium has been found to be between 4 and 5 (Chen et al., 1973a; Huang, 1975). When soil pH was below 3, soluble complexes of phosphorus with monomeric Al^{3+} ions were released from the oxide lattice. With increase in pH under conditions where Al^{3+} is already hydrolysed, complexes of phosphate with hydroxy-Al ions will be more firmly adsorbed (White and Thomas, 1981). If the pH increases higher than 6.5 - 7, $Al(OH)_3$ becomes more stable than $AlPO_4$ and is therefore the preferred form. Hence, the

availability of phosphate in the soil solution will not decline within this pH range (White, 1981).

In order to explain a decrease of soil solution phosphorus concentration corresponding to an increase in soil pH and/or ionic strength of soil solution, Robarge and Corey (1979) studied the adsorption of phosphorus by hydroxy-Al species on a cation exchange resin. They pointed out that the reduction of solution phosphorus concentration was associated with the formation of a new P-adsorbing surface in the form of sites of exchangeable Al^{3+}. They also suggested that there was a positive correlation between phosphorus adsorption and exchangeable aluminium because of the relationship between Al^{3+} and the formation of hydroxy-Al species. The relationship was dependent on the condition that the rate at which phosphorus was added was not so high as to bring about precipitation of phosphorus in the form of an aluminium-phosphate compound.

Harter (1969) studied phosphorus adsorption sites in various soils and revealed that organic matter was crucial in the primary bonding of phosphorus. He also claimed that the primary bonding sites for phosphorus were specific anion exchange sites (e.g. hydroxyl ions) on organic matter. Subsequent adsorption involving aluminium and iron cations resulted in the formation of less soluble aluminium and iron phosphates. The release of P from the sites of initial adsorption was possible when the concentration of P in the soil solution decreased.

Complex organic anions with carboxyl groups may be involved in similar reactions with phosphate anions in highly weathered soils. Inoue and Wada (1971) demonstrated that adsorption of organic material by "allophane" (amorphous aluminosilicates) was effected by ligand exchange of the oxygen of carboxylic groups with structural oxygen co-ordinated with aluminium. The similarity of reactions of both soil organic matter and phosphorus with aluminium and iron suggest that addition of organic material such as crop residues or manure may reduce phosphorus sorption and thus increase fertilizer efficiency in these soils.

More specifically Deb and Datta (1967) showed that of various organic anions (e.g. citrate, tartrate, and oxalate) citrate reacted most effectively with soil constituents to reduce their reactivity with phosphate which thus remained free in solution. This is in agreement with results obtained by Nagarajah et al. (1970) using kaolinite and oxide surfaces (i.e. gibbsite and goethite). They found, in accord with findings on detoxifying effects of organic acids, that citrate and oxalate were very effective in decreasing phosphate sorption; tartrate, malonate, and malate were moderately effective; and acetate, lactate, and succinate had little effect. In addition, polygalacturonate markedly decreased phosphate sorption, particularly on kaolinite but monomer galacturonate did not.

On the other hand, Appelt et al. (1975b) found that addition of humic and fulvic acids to volcanic soils high in "allophane" did not reduce phosphorus sorption because complex formation between humic acid and Al ions extracted from the "allophane" did not block P adsorption sites on these soils but created new reactive sites for P adsorption. Also, Bloom (1981) showed that sorption of phosphate by an aluminium-peat complex was due to sorption of complex aluminium-phosphate cations by the peat and the precipitation of amorphous Al-hydroxy-phosphate [e.g. $AlH_2PO_4(OH)_2$].

Yuan (1980) showed that the effect of organic matter on phosphorus retention by soils can be positive or negative depending on soil properties including particle size distribution, type and content of clay minerals, and the capacity for phosphorus and/or organic matter adsorption. For instance, soils containing very high contents of free sesquioxide and kaolinite clay would be expected to adsorb phosphorus strongly (e.g., krasnozem), whereas soils with very low free sesquioxide content and dominantly illitic clay would be expected to show low retention of phosphorus (Deb and Datta, 1967). Yuan (1980) also stated that sites for organic matter and phosphorus sorption may be different, but that certain sites may sorb both phosphorus and organic matter. Since P may block only some of the adsorption sites

available for sorption of organic material, the adsorption sites for organic matter may not be totally the same as for P.

2 GENERAL MATERIALS AND METHODS

In this chapter, the experimental materials and methods common to experiments in the following chapters will be described.

2.1 Soil and Soil Preparation

The soils used in the experiments were from the top 15 cm (A horizon) of 'acid red loam' krasnozems developed on basalt in the hinterland of the North West Coast of Tasmania. The soils were brought to Hobart in moist condition where they were passed through a 5 mm sieve to remove plant materials and gravel before being air dried. The air-dried soils were sieved through a round-holed International 2 mm sieve and stored in galvanized steel bins. Some chemical properties of the air-dried soils were determined as described in section 2.5.

2.2 Organic Matter

The two organic materials used were lucerne chaff (Medicago sativa L.) and barley straw (Hordium vulgaris L.) which were assumed to be of low C/N ratio (18.7) and high C/N ratio (104.1) respectively. They were air dried, ground to pass a 2 mm sieve and stored in plastic bags.

2.3 Test Plant

The plant grown throughout this study was perennial ryegrass, Lolium perenne L. cultivar 'Nui' obtained from the Department of Agriculture, Tasmania.

2.4 Glasshouse Conditions

Soils were incubated and plants were grown in a glasshouse at the University of Tasmania, Hobart. Relative humidity was controlled above 50% by the injection of water sprays into the air stream and temperature was maintained generally above 10 °C at night and below 30 °C during the day. Temperature was controlled by the air stream which was heated by an oil-fired furnace or cooled by refrigeration as required. The air flow and the change rate were controlled to provide a minimum of 20 changes/hour. Natural light only was used and day length varied from a minimum of 9 hours in winter to a maximum of 15 hours in summer.

2.5 Soil Analysis

2.5.1 Soil reaction (pH)

pH was determined using a 1:5 (w/v) mixture of soil and $BaCl_2$ (0.002 M) solution after shaking for 16 hours (Gillman and Sumpter, 1986). A Beckman 44 pH meter with a combined glass and calomel electrode was used to measure the pH of the suspension 1 minute after immersion of the electrode.

2.5.2 Ionic strength

Soil solution ionic strength was estimated by measuring the electrical conductivity of a 1:5 soil-water suspension after shaking for 16 hours. The ionic strength (I.S.) of the soil solution at field capacity was calculated by using the formula of Gillman and Bell (1978):

$$I.S. = 0.0446\ C - 0.000173$$

where C is the electrical conductivity in mS cm^{-1}.

2.5.3. Sum of basic exchangeable cations (ΣBEC) and cation exchange capacity (CEC)

The method used for determination of ΣBEC and CEC of soils was that described by Gillman and Sumpter (1986). Calcium and magnesium were determined using an atomic absorption spectrophotometer (AAS) while potassium and sodium were measured using a flame photometer.

The atomic absorption spectrophotometer was a Pye Unicam Model SP-1800. Acetylene and air were used as the fuel and the oxidant respectively. Analyses were based on an integration time of 1 sec. and the mean of 10 analyses was recorded for each sample. Operating conditions for each element are shown in Table 2.1 .

Table 2.1. Operating conditions for Pye Unicam SP1800 atomic absorption spectrophotometer

Element	Wavelength (nm)	Slitwidth (mm)	Lamp Current (mA)	Burner Height (cm)	Fuel Flow Rate (min^{-1})	Oxidant Flow Rate (min^{-1}) Air
Ca	422.7	0.20	8	0.8	1.4	5
Mg	285.2	0.20	4	0.5	1.4	5

The AAS was run approximately 20 min before the commencement of analysis to ensure stability. Blanks (duplicate) and standards were analysed at the beginning and end of a run of unknown samples to minimize the error associated with drift. The drift from the start to the end of a run rarely exceeded 5%. During the course of a run, readings for standards were checked periodically as an additional check. Deionized water was run through the atomizer between samples to eliminate contamination.

The flame photometer was an EEL type (Evans Electroselenium Ltd., Hallstead, Essex, England). Optical filters isolated the characteristic wavelength bands of the two elements from the emitted light. Propane and air were used as the fuel and the oxidant, respectively. The air was pumped into the burner at a constant pressure of 0.69 bar. Deionized water was run through the atomizer between samples to eliminate contamination.

In the calcium and magnesium determinations, possible interference due to aluminium, phosphate and silicate was overcome by using strontium as suggested by G.P. Gillman (personal comm.). Ca and Mg were determined after a 20-fold dilution of the original extract. For K and Na, a 10-fold dilution of the original extract was required. The contents of Ca, Mg, K and Na were calculated from a

standard curve prepared within the concentration ranges of 0-1.0 me/l for Ca and 0-0.2 me/l for Mg, K and Na.

2.5.4 Available phosphorus

Phosphorus was extracted by shaking 1 g. of soil in 20 ml of 0.5 M $NaHCO_3$ at pH 8.5 for 16 hours in a 25 °C room (Olsen and Sommers, 1982). Phosphorus-free carbon black was added to obtain a clear filtrate. The suspension was filtered through Whatman No.42 filter paper. Phosphorus in the extract was determined as the molybdenum blue complex using ascorbic acid as reductant in the presence of antimony (Murphy and Riley, 1962). The analyses were made with a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 882 nm. This phosphorus fraction was termed "available phosphorus".

2.5.5 Exchangeable aluminium

Exchangeable aluminium was extracted by shaking 1 g. of soil in 10 ml of 1M KCl for 16 hours and then filtering through Whatman No.42 filter paper (Barnhisel and Bertsch, 1982). Aluminium in the extract was measured by the aluminon method (Hsu, 1963) using ascorbic acid to minimize iron interference (Jayman and Sivasubramaniam, 1974).

3 SOME EFFECTS OF ADDED ORGANIC MATTER ON PROPERTIES OF KRASNOZEM TOPSOILS FROM NORTH WEST TASMANIA

3.1 Introduction

Many Tasmanian soils have formed in materials that have been highly weathered and strongly leached so that the soils are moderately to strongly acid and their base status is relatively low (Nicolls and Dimmock, 1965). The highly valued krasnozem on basalt in northern Tasmania are typical.

Under agricultural uses in which crop or animal product is removed it is necessary to compensate for further loss of bases by liming, preferably managed in relation to composition of the soil exchange complex to ensure a satisfactory balance of calcium versus magnesium, especially where there are also inputs of potassium. Without such inputs further acidification may be associated with increased activity of monomeric soil aluminium.

On the other hand the cost of liming is such that cheaper alternatives for management of the level of monomeric soil aluminium would offer significant economic benefit. Soil organic matter is known to form stable complexes with aluminium so that management conducive to maintenance of a higher level of organic matter in cropped soils may allow reduced frequency of liming.

The aim of the present experiment was to find out the effect of different types and rate of application of organic matter (O.M.) on certain properties of acid krasnozems collected from N.W. Tasmania. The soil properties studied included soil reaction (pH), soil solution ionic strength, sum of basic exchangeable cations (ΣBEC), cation exchange capacity (CEC), bicarbonate-extractable (available) P and exchangeable Al. It was intended to use the results of this experiment in selecting the most suitable soil for further study of the effectiveness of O.M. on Al stress in relation to soil P and plant growth.

3.2 Materials and Methods

3.2.1 Experimental design

The variables in this experiment were:

Variable 1 (main plots) three soil series viz., Burnie, Lapoinya and Yolla.

Variable 2 (subplots) two kinds of organic matter viz., barley straw (Hordium vulgaris L.) and lucerne chaff (Medicago sativa L.)

Variable 3 (sub-subplots) three rates of organic matter viz., 0, 6.2 and 12.4 g/pot (equivalent to 0, 3.5, 7.0 t/ha)

Treatments were arranged in a split-split plot design with 3 replications. The positions of the pots on the glasshouse benches were re-randomized every week to minimize any local environmental effects.

3.2.2 Soils

The three soil materials used in this experiment were the A horizons to 15 cm depth of a topographic sequence of `acid red loams´ or krasnozems developed on basalt extending from the coast upwards in elevation to the tiers of North West Tasmania. This sequence included the Burnie, Lapoinya and Yolla series (Loveday and Farqular, 1958) from lowest to highest elevation, respectively. The soils were collected from the Forthside Vegetable Research Station, Elliott Research Station and the Tewkesbury Potato Breeding Station respectively, all of which are operated by the Tasmania Department of Agriculture. The soils from which specimens were collected had a long history of cultivation including addition of fertilizer. At the time of sampling, they were under a cover of pasture or weeds. After arrival at the Department of Agricultural Science of Tasmania, Hobart, the soils were air dried and prepared as in Section 2.1 above. Some chemical properties of these soils are given in Table 3.1

3.2.3 Incubation of soils and soils plus organic matter

Subsamples of the three soils were each thoroughly mixed with one of two types of organic matter (O.M.) (lucerne chaff and barley straw) which were prepared as desecribed in Section 2.2. Three rates of organic matter were used, viz.,

Table 3.1 Chemical and physical properties of the A horizon of three Krasnozems

Determination	Soil Series			Method
	Burnie (S1)	Lapoinya (S2)	Yolla (S3)	
Available P($\mu g\ g^{-1}$)	57.2	86.6	83.6	Olsen&Sommers, 1982; Murphy&Riley, 1962
P adsorption($\mu g\ g^{-1}$)	932.13	977.38	1065.44	Soil Testing Service Method and interpretation, Dept. of Agri., N.S.W..
Al (KCl) ($\mu g\ g^{-1}$)	110.6	91.3	100.8	Barnhisel&Bertsch(1982) Hsu(1963)
Total N (%)	0.21	0.24	0.26	Kjeldahl Method
Organic C (%)	5.01	6.5	11.96	Walkley&Black
pH (0.002M $BaCl_2$), 1:5	4.5	4.5	4.7	Gillman&Sumpter (1986)
Ionic strength (soil solution)	3.8×10^{-3}	3.5×10^{-3}	4.5×10^{-3}	Gillman&Bell (1978)
CEC(meq100 g^{-1}soil)	12.21	10.66	14.42	Gillman&Sumpter(1986)
Ca (meq100 g^{-1}soil)	8.5	8.4	10.78	
Mg (meq100 g^{-1}soil)	0.8	0.7	1.9	
Na (meq100 g^{-1}soil)	0.15	0.17	0.16	
K (meq100 g^{-1}soil)	0.8	0.6	0.8	
Moisture content at F.C.(pF2)(mg g^{-1})	423	484	572	
Sand (%) #	12.6	7.0	8.0	CSIRO ,Div. of Soils,
Silt(%) #	23.4	24.4	24.1	Tas. Regional Lab.
Clay(%) #	60.4	65.0	67.5	(unpublished)
Field texture	clay loam	clay loam	clay loam	

These data are representative but are from different sites to those of the present soils

0, 6.2, and 12.4 g/pot (150 mm diameter) equivalent to 0, 3.5, and 7 t/ha, the highest rate being typical of a normal field application in Tasmanian agriculture (Yates, J.J., pers. comm.). The mixtures were placed in black polythene pots (diameter 150 mm, height 178 mm). The pot contents were brought to their field capacity moisture content and this was maintained by weighing the pots daily and adding deionized water as needed. To prevent rapid drying the pots were covered with plastic food wrap with small holes pricked in it for aeration. The pots were incubated in the glasshouse for four weeks. At the end of the incubation period, the pot contents were air dried, passed through a 2 mm sieve and stored at 4 ^{o}C before chemical analysis.

3.2.4 Soil analysis

The following determinations were made on subsamples from each pot.

Soil reaction: pH was measured in 0.002 M $BaCl_2$ using a soil to solution ratio of 1:5 (Gillman and Sumpter, 1986).

Sum of basic exchangeable cations (∑BEC) and cation exchange capacity (CEC): ∑BEC and CEC of the soils were determined by the method of Gillman and Sumpter (1986). Ca and Mg in the extracts were measured using an atomic absorption spectrophotometer (AAS). K and Na were determined by flame photometer.

Ionic strength: soil solution ionic strength was estimated by measuring the electrical conductivity of a 1:5 soil-water suspension (Gillman and Bell, 1978).

Available phosphorus: bicarbonate-extractable phosphorus (designated "available P") was extracted by shaking a 1:20 mixture of soil and 0.5 M $NaHCO_3$ (pH 8.5) for 16 hours in a constant temperature room maintained at 25±1 ^{o}C (Olsen and Sommers, 1982). P was analysed using the colorimetric method developed by Murphy and Riley (1962).

Exchangeable aluminium: exchangeable Al was extracted by shaking a 1:10 (soil/extractant) suspension of soil in 1 M KCl for 16 hours (Barnhisel

and Bertsch, 1982). Al was determined by the aluminon method (Hsu, 1963; Jayman and Sivasubramaniam, 1974).

Further details of these soil analytical methods have been given in Chapter 2, Section 2.5 above.

3.3 Results and Discussion

3.3.1 Sum of basic exchangeable cations (∑BEC) and cation exchange capacity (CEC)

The ∑BEC and CEC of Yolla soil was higher ($P<0.001$) than Burnie and Lapoinya soils but there was no significant difference between the Burnie and Lapoinya soils. This reflected the intrinsic differences between the soils. There was no significant effect ($P>0.05$) of added O.M. over the range tested. The data are given in Figures 3.1 and 3.2, Tables 3.2 and 3.3, and Appendix 3.1. The results were in accord with data for the untreated soils (Table 3.1) where it may be seen that the Walkley-Black carbon content of the Yolla soil was about twice that of the Burnie and Lapoinya soils and that the CEC of Yolla soil was also significantly higher. Soil O.M. has a great influence in reducing the point of zero charge of soils of variable charge, thus enhancing CEC, and in the case of the Yolla soil its ability to retain basic nutrient cations against leaching loss (Gillman, 1985). The initial pH of Yolla soil was higher than for the Burnie and Lapoinya soils further indicating the higher negative charge of the Yolla soil .

The effects on ∑BEC of the addition of lucerne chaff compared with barley straw to the three soils were significantly different ($P<0.05$) but there were only slight effects ($P=0.065$) on CEC. This may be due to the composition of lucerne chaff and its lower C/N ratio as compared with barley straw which would be expected to support a greater activity of soil microorganism in its decomposition than barley straw. Greater release of organic anions from such decomposition should also decrease the point of zero charge of variable charge components of the soil.

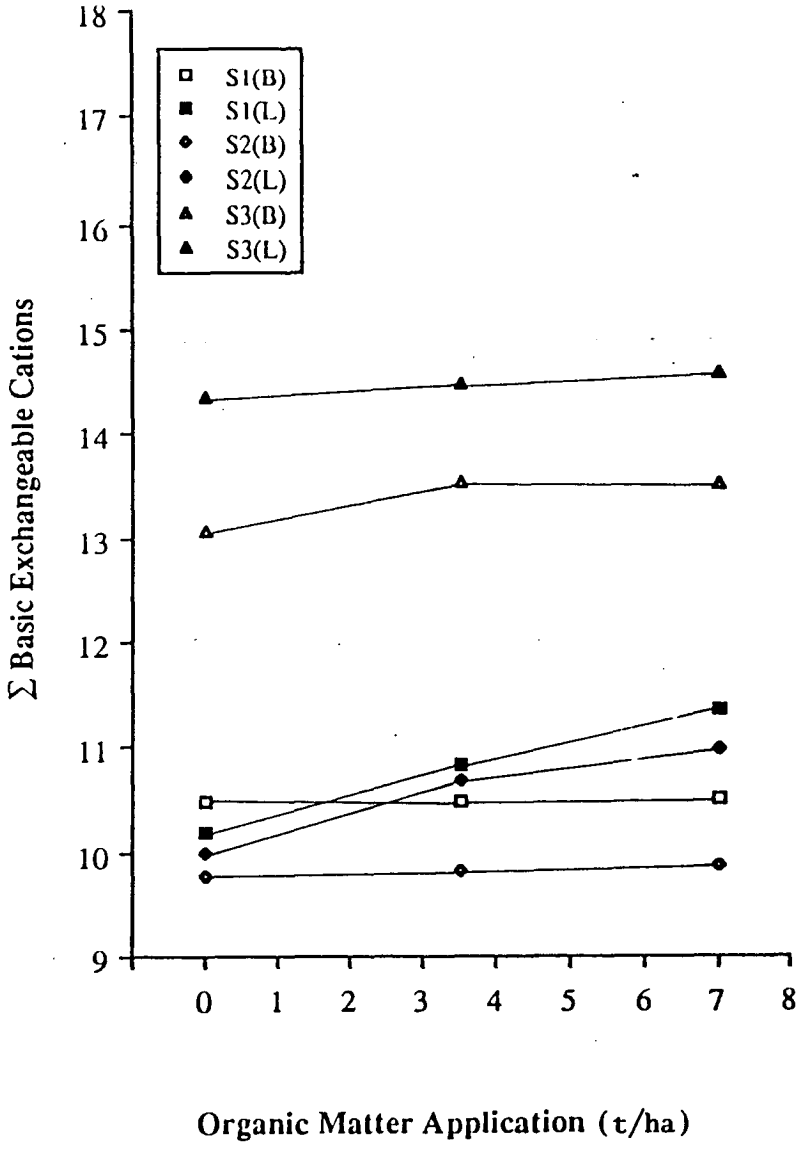


Figure 3.1 Effects of added organic matter (Barley straw, B, or lucerne chaff L, at 0, 3.5, 7.0 t/ha) on the sum of basic exchangeable cations in three A horizons (Burnie-S1, Lapoinya-S2, and Yolla-S3)

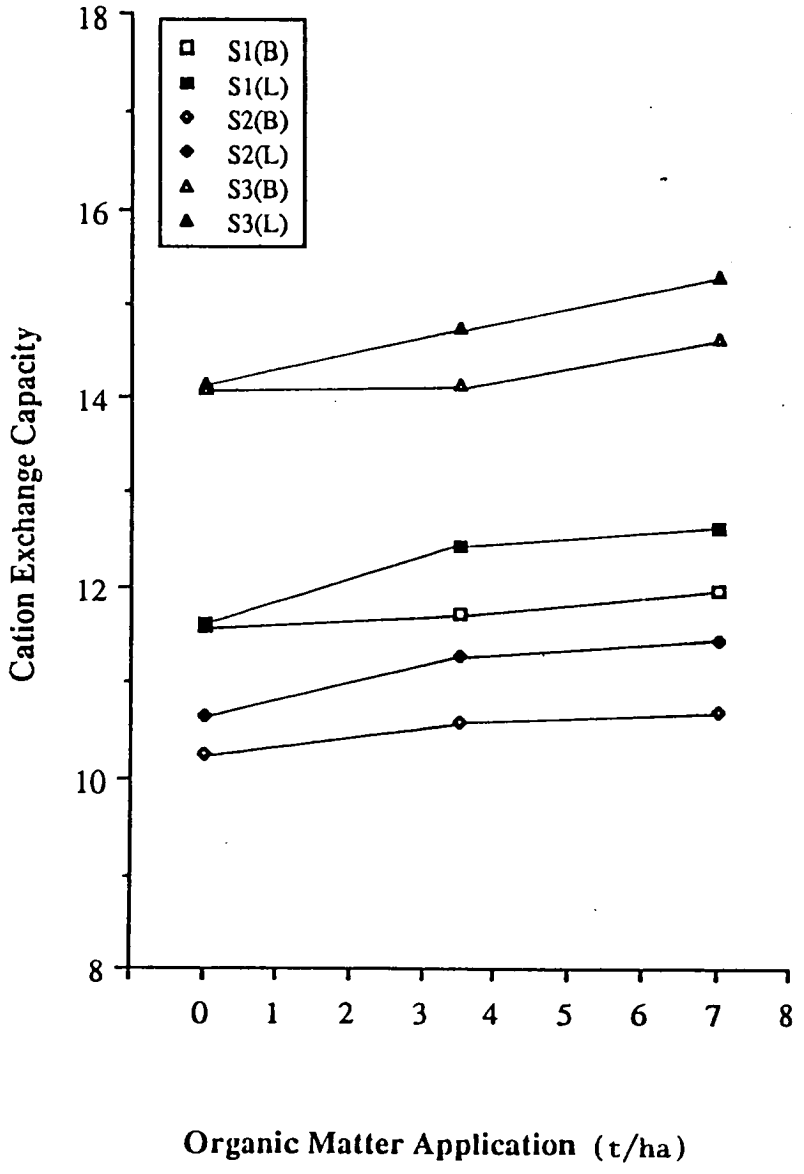


Figure 3.2 Effects of added organic matter (Barley straw, B, and Lucerne Chaff, L, at 0, 3.5, 7.0 t/ha) on cation exchange capacity in three A horizons (Burnie-S1, Lapoinya-S2, and Yolla-S3)

Table 3.2 ΣBEC (meq $100g^{-1}$soil) for soil series, and type and rate of organic matter application (Means of three replications).

i. Soil series (S) x O.M. rate (R)

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	10.34	10.66	10.93	10.64
Lapoinya soil(S2)	9.89	10.25	10.42	10.19
Yolla soil(S3)	13.71	14.0	14.05	13.92
mean (R)	11.31	11.64	11.8	

LSD (0.05); Soil series (S) = 0.57 *** S x R = NS
O.M. rate (R) = NS

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	11.12	11.28	11.3	11.23
Lucerne chaff(L)	11.51	12.0	12.31	11.94

LSD (0.05); O.M. type (T) = 0.66 * T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	10.50	10.79	10.64
Lapoinya soil(S2)	9.82	10.56	10.19
Yolla soil(S3)	13.37	14.47	13.92

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	10.5	10.49	10.51	10.19	10.83	11.36
Lapoinya soil(S2)	9.78	9.82	9.86	10.0	10.69	10.99
Yolla soil(S3)	13.07	13.53	13.52	14.35	14.47	14.58

LSD (0.05); S x T x R = NS

NS, *, **, *** : Non significant, significant at 0.05, 0.01 and 0.001, respectively.

Table 3.3 CEC (meq $100g^{-1}$ soil) in relation to soil series, type of added organic matter and rate of organic matter application (Means of three replications).

i. Soil series (S) x O.M. rate (R):

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	11.58	12.08	12.30	11.99
Lapoinya soil(S2)	10.46	10.93	11.07	10.83
Yolla soil(S3)	14.11	14.45	14.97	14.51
mean (R)	12.06	12.49	12.78	

LSD (0.05); Soil series (S) = 1.17 *** S x R = NS
O.M. rate (R) = NS

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	11.97	12.15	12.45	12.19
Lucerne chaff(L)	12.13	12.83	13.12	12.69

LSD (0.05); O.M. type (T) = NS T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	11.76	12.22	11.99
Lapoinya soil(S2)	10.52	11.13	10.82
Yolla soil(S3)	14.29	14.74	14.51

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	11.57	11.73	11.98	11.60	12.44	12.62
Lapoinya soil(S2)	10.27	10.58	10.71	10.65	11.29	11.44
Yolla soil(S3)	14.08	14.14	14.65	14.15	14.76	15.30

LSD (0.05); S x T x R = NS

3.3.2 Ionic strength of soil solution (I.S.)

The cation and anion exchange capacity of highly weathered soils dominated by Fe- and Al- oxides and 1:1 type aluminosilicate clay minerals depends mainly upon the ionic strength (I.S.) of the soil solution (van Raij and Peech, 1972; El-Swaify and Sayegh, 1975; Gillman and Bell, 1976). The data for I.S. in this experiment were in accordance with those for CEC and ΣBEC for the three soils used. Application of organic matter had significant effects ($P<0.01$) on soil solution ionic strengths in the three different soils. Lucerne chaff had a greater effect ($P<0.05$) on I.S. than barley straw. Also the I.S. of the soil solution increased ($P<0.001$) with rate of organic matter application. The data are summarized in Figure 3.3; Table 3.4 and full details are given in Appendix 3.2.

3.3.3 Available phosphorus

The three soils had different levels of available P ($P<0.001$) after incubation. The Lapoinya soil was highest followed by Yolla and Burnie soils. (Figure 3.4; Table 3.5; Appendix 3.3).

Addition of organic matter at both levels increased ($P<0.01$) available P compared with the controls. This may be due to release of P, during the partial decomposition of organic matter, above the requirements of microorganisms. There was no significant effect of kind of organic matter on levels of available phosphorus. Such effects depend not only on composition of organic matter, but on environmental conditions and activity of soil microorganisms. It has been reported that fresh organic matter has a priming effect on decomposition of native humus, with mineralization of organic phosphorus (Stevenson, 1982). The present results are in accord with the report of van Diest and Black (1959) that phosphorus present in organic forms at the beginning of a season contributed substantially to plant nutrition in that season. Similar results were obtained by Saunders and Metson (1971) and Dormaar (1972).

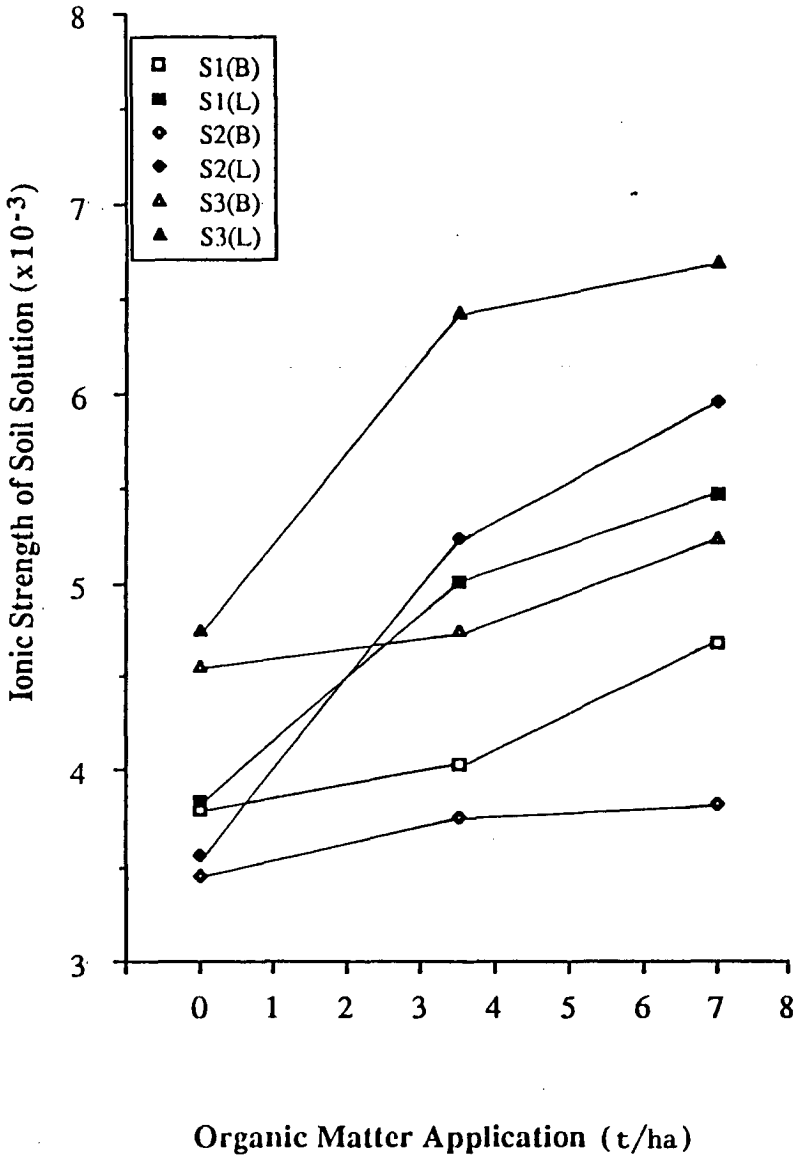


Figure 3.3 Effects of added organic matter (Barley straw, B, and Lucerne Chaff, L, at 0, 3.5, 7.0 t/ha) on ionic strength of soil solution in three A horizons (Burnie-S1, Lapoinya-S2, and Yolla-S3)

Table 3.4 Ionic strength of soil solution (Gillman and Bell, 1978) in relation to soil series, type of added organic matter and rate of organic matter application (Means of three replications x 10^{-3}).

i. Soil series (S) x O.M. rate (R):

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	3.82	4.52	5.08	4.47
Lapoinya soil(S2)	3.52	4.50	4.89	4.30
Yolla soil(S3)	4.65	5.59	5.97	5.41
mean (R)	4.0	4.87	5.31	

LSD (0.05); Soil series (S) = 0.48 ** S x R = NS
O.M. rate (R) = 0.53 ***

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	3.93	4.18	4.58	4.23
Lucerne chaff(L)	4.05	5.56	6.04	5.22

LSD (0.05); O.M. type (T) = 0.74 * T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	4.17	4.78	4.48
Lapoinya soil(S2)	3.68	4.92	4.3
Yolla soil(S3)	4.85	5.96	5.41

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	3.79	4.03	4.68	3.84	5.0	5.48
Lapoinya soil(S2)	3.46	3.75	3.83	3.57	5.24	5.96
Yolla soil(S3)	4.55	4.75	5.24	4.75	6.44	6.69

LSD (0.05); S x T x R = NS

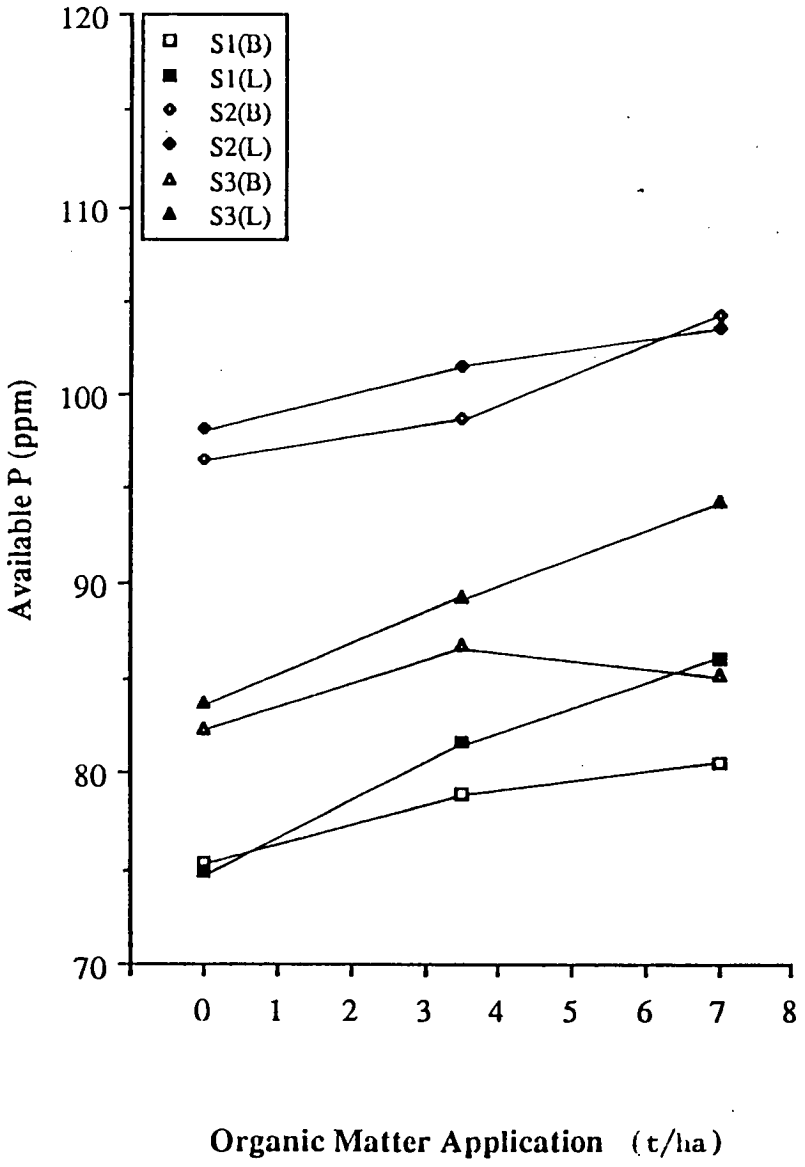


Figure 3.4 Effects of added organic matter (Barley straw, B, and Lucerne Chaff, L, at 0, 3.5, 7.0 t/ha) on available P in three A horizons (Burnie-S1, Lapoinya-S2, and Yolla-S3)

Table 3.5 Available phosphorus (μgPg^{-1}soil) in relation to soil series, and type and rate of organic matter application (Means of three replications).

i. Soil series (S) x O.M. rate (R):

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	75.12	80.31	83.33	79.58
Lapoinya soil(S2)	97.42	100.11	103.98	100.5
Yolla soil(S3)	83.09	88.09	89.78	86.98
mean (R)	85.21	89.5	92.36	

LSD (0.05); Soil series (S) = 4.58 *** S x R = NS
O.M. rate (R) = 4.11 **

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	84.78	88.16	90.04	87.66
Lucerne chaff(L)	85.64	90.84	94.69	90.39

LSD (0.05); O.M. type (T) = NS T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	78.26	80.91	79.58
Lapoinya soil(S2)	99.87	101.14	100.50
Yolla soil(S3)	84.85	89.12	86.98

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	75.34	78.89	80.55	74.89	81.72	86.11
Lapoinya soil(S2)	96.56	98.72	104.33	98.29	101.5	103.63
Yolla soil(S3)	82.45	86.87	85.24	83.73	89.30	94.32

LSD (0.05); S x T x R = NS

3.3.4 Exchangeable aluminium

The level of exchangeable Al in the Burnie soil was greater ($P<0.001$) than in the Yolla soil which was in turn greater than in the Lapoinya soil (Figure 3.5, Table 3.6, Appendix 3.3). Addition of organic matter and incubation caused reduced levels of exchangeable aluminium in each of the soils. The effects were similar regardless of initial levels of exchangeable aluminium in the soils (Table 3.1). The present results are in accord with the production of chelants during organic matter decomposition, with immobilization of aluminium, together with the possibility of formation of insoluble compounds with phosphate as proposed by Stevenson (1982).

3.3.5 Soil reaction (pH)

There were no significant pH changes in response to organic matter addition in the form of either barley straw or lucerne chaff at any level of application (Figure 3.6; Table 3.7; Appendix 3.2). This may suggest that the rates of organic matter application were not high enough to affect soil pH although other soil properties were affected. Hoyt and Turner (1975) reported that pH changed as incubation time increased after the application of a large amount of organic matter to acid soils. Similar results were obtained by Ritchie and Dolling (1985). They suggested that soil pH increased during decomposition of organic matter when soil moisture was held at field capacity due to the increased release of organic anions with time of incubation or to their adsorption on soil surfaces. The failure of increased I.S. to lower pH could be a counteracting effect to the release of organic anions and their tendency to increase pH.

3.3.6 Conclusion

The results obtained in the present experiment showed positive effects of added organic matter on all three soils used. However, the effects were relative to the initial levels of the soil properties examined. There were no markedly different effects due to type of organic matter. Although the addition of organic matter had significant effects on decreasing exchangeable Al and on increasing available P and soil solution ionic strength. However, there were no significant differences in effects

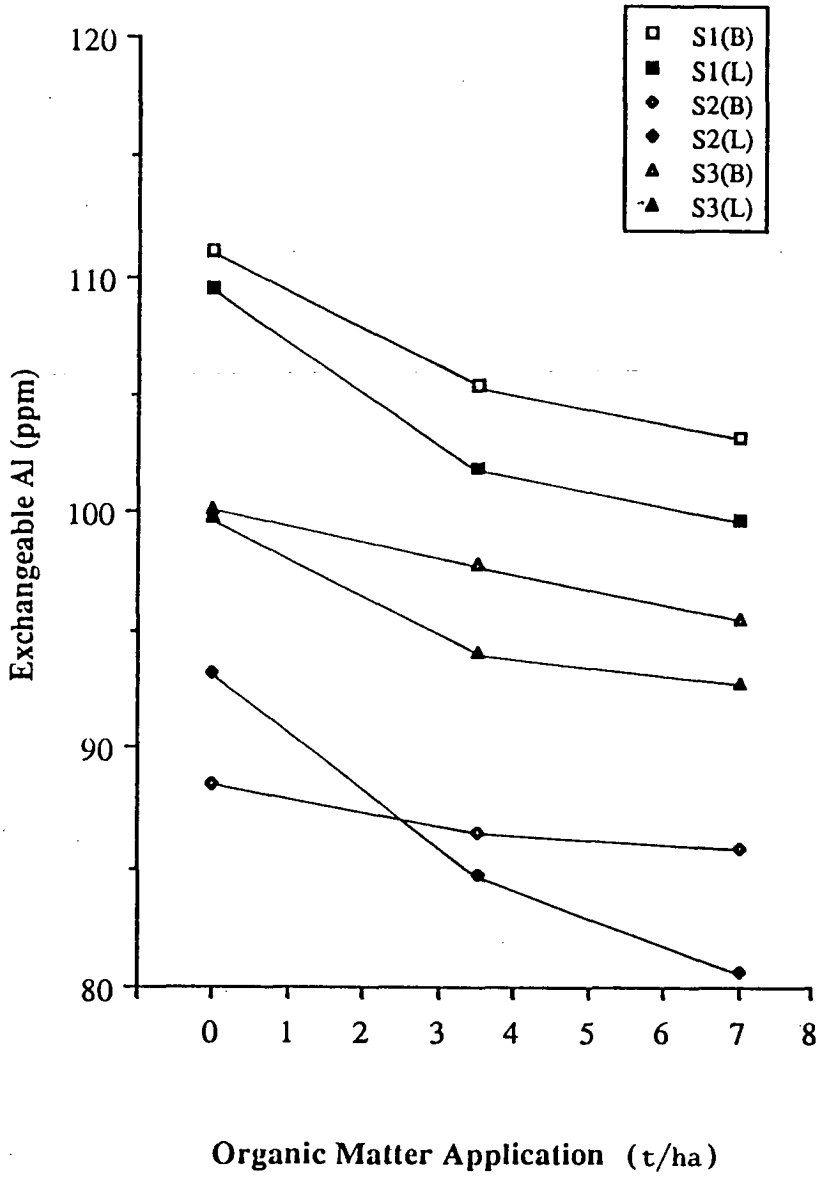


Figure 3.5 Effects of added organic matter (Barley straw, B, and Lucerne Chaff, L, at 0, 3.5, 7.0 t/ha) on exchangeable Al in three A horizons (Burnie-S1, Lapoinya-S2, and Yolla-S3)

Table 3.6 Exchangeable Al (μg g^{-1}soil) in relation to soil series, type and rate of organic matter application (Means of three replications).

i. Soil series (S) x O.M. rate (R):

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	110.32	103.67	101.46	105.15
Lapoinya soil(S2)	90.83	85.61	83.28	86.57
Yolla soil(S3)	100.03	95.97	94.16	96.72
mean (R)	100.39	95.08	92.97	

LSD (0.05); Soil series (S) = 2.26 *** S x R = NS
O.M. rate (R) = 2.9 ***

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	99.93	96.58	94.86	97.12
Lucerne chaff(L)	100.86	93.58	91.07	95.17

LSD (0.05); O.M. type (T) = NS T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	106.58	103.72	105.15
Lapoinya soil(S2)	86.94	86.20	86.57
Yolla soil(S3)	97.85	95.58	96.72

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	111.12	105.42	103.21	109.52	101.93	99.71
Lapoinya soil(S2)	88.45	86.52	85.85	93.21	84.69	80.71
Yolla soil(S3)	100.22	97.81	95.53	99.84	94.13	92.78

LSD (0.05); S x T x R = NS

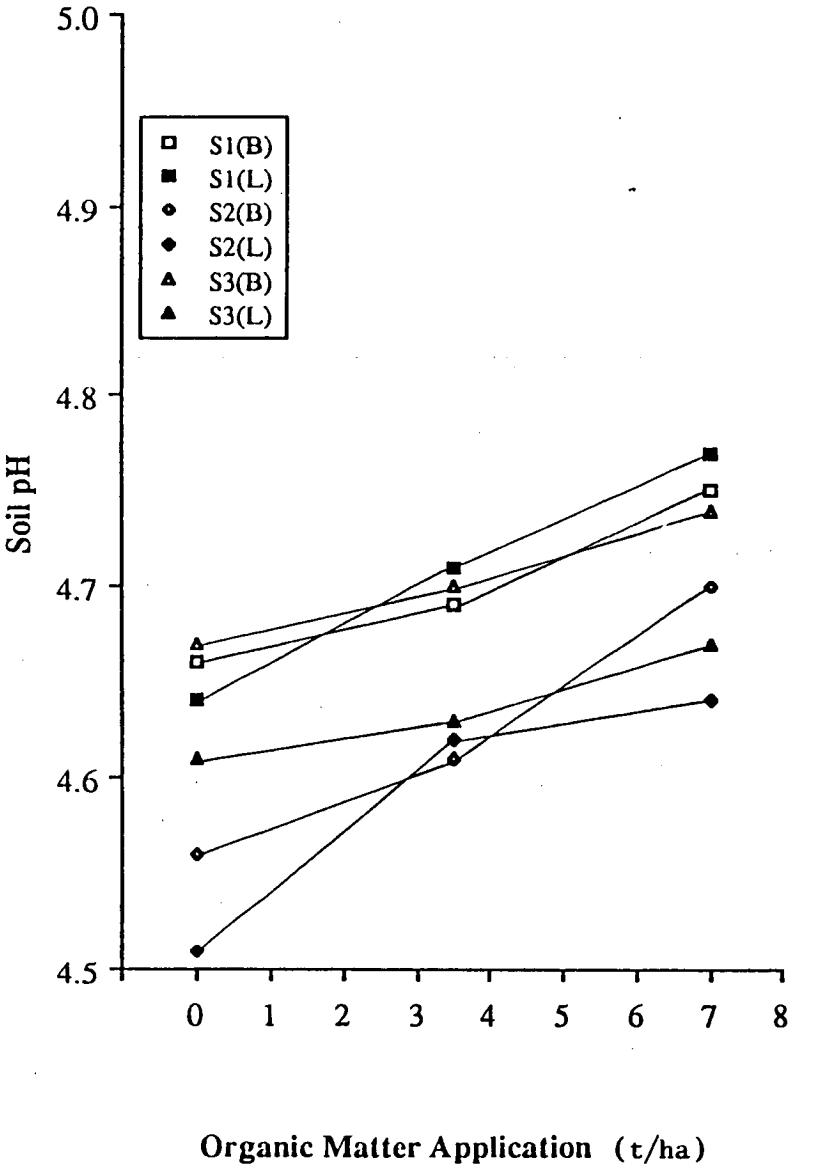


Figure 3.6 Effects of added organic matter (Barley straw, B, and Lucerne Chaff, L, at 0, 3.5, 7.0 t/ha) on soil pH in three A horizons (Burnie.S1, Lapoinya.S2, and Yolla S3)

Table 3.7 pH of untreated soils in relation to type and rate of organic matter application (Means of threee replications)

i. Soil series (S) x O.M. rate (R)

(Rate: ton/ha)	0	3.5	7.0	mean
Soil series				
Burnie soil(S1)	4.65	4.70	4.76	4.70
Lapoinya soil(S2)	4.54	4.62	4.67	4.61
Yolla soil(S3)	4.64	4.67	4.71	4.67
mean (R)	4.61	4.66	4.71	

LSD (0.05); Soil series (S) = NS S x R = NS
O.M. rate (R) = NS

ii. O.M. type (T) x O.M. (R)

(Rate: ton/ha)	0	3.5	7.0	mean
O.M. type				
Barley straw(B)	4.63	4.67	4.73	4.68
Lucerne chaff(L)	4.59	4.65	4.69	4.64

LSD (0.05); O.M. type (T) = NS T x R = NS

iii. Soil series (S) x Organic matter type (T)

O.M. type	Barley straw	Lucerne chaff	mean
Soil series			
Burnie soil(S1)	4.70	4.71	4.70
Lapoinya soil(S2)	4.62	4.59	4.61
Yolla soil(S3)	4.70	4.64	4.67

LSD (0.05); S x T = NS

iv. Soil series (S) x O.M. type (T) x O.M. rate (R)

O.M. type	Barley straw			Lucerne chaff		
O.M. rate	0	3.5	7.0	0	3.5	7.0
Soil series						
Burnie soil(S1)	4.66	4.69	4.75	4.64	4.71	4.77
Lapoinya soil(S2)	4.56	4.61	4.70	4.51	4.62	4.64
Yolla soil(S3)	4.67	4.70	4.74	4.61	4.63	4.67

LSD (0.05); S x T x R = NS

on CEC, ΣBEC and pH in relation to type of organic matter. Therefore, it may be suggested that the conventional rate of organic matter application (7 t/ha) may be just enough to improve soil properties in the short term, with regular applications to replenish decomposed organic materials in order to sustain beneficial effects.

Finally, the Burnie series soil was chosen for further studies because it had the highest level of exchangeable Al and the lowest level of organic carbon. In addition it had the lowest level of available P, the lowest P sorption capacity, was strongly acid in reaction and there was no organic matter x soil interaction.

4. EFFECTS OF ORGANIC MATTER ADDED TO AN ACID KRASNOZEM AFTER DIFFERENT PERIODS OF INCUBATION, WITH AND WITHOUT ADDED UREA, ON SOIL ALUMINIUM, PHOSPHORUS, AND IONIC STRENGTH OF SOIL SOLUTION

4.1. Introduction

Nitrogen content of plant materials is well known to be an important factor controlling the rate of organic matter decomposition (Aber and Melillo, 1980; Cowling and Menill, 1966). The addition of supplementary N to natural litter materials (Mahendrappa, 1978) and incorporated crop residues can accelerate their rate of decomposition (Allison and Cover, 1960; and Bartholomew, 1965). Organic compounds produced in the decomposition process are capable of forming complexes with metals such as Al and Fe. Mechanisms include surface adsorption, chelation, or other complex reactions (Mortensen, 1963; Cabrera and Talibudeen, 1977).

However, the effects of organic material added to acid soils after different periods of incubation, with and without supplementary Urea-N, on soil P and Al in acid soils have not been studied, particularly on this soil. The objectives of this experiment were, therefore to examine such effects on available P (0.5 M $NaHCO_3$ extractable at pH 8.5), exchangeable Al (1 M KCl extractable), soil pH (1:5 w/v in 0.002 M $BaCl_2$) and ionic strength (I.S.) of soil solution, under glass house conditions. And also to find out the suitable rate of organic matter application to improve such soil properties.

4.2. Materials and Methods

4.2.1. Experimental design

The variables studied in this experiment were kind and level of added organic matter and rate of applied urea. A split-split plot design was used with three replications:

Variable 1 (main plots): Two kinds of organic matter, barley straw (B) and lucerne chaff (L)

Variable 2 (subplots): Two rates of urea application based on C/N ratio of the applied organic matter; (a) without urea application (No), and (b) with enough urea to bring the C/N ratio of the added organic matter to a value of 12 (N1) (Table 4.1).

Variable.3 (sub-subplots): Three rates of organic matter application, 0 (0), 80 (1), and 160 (2) g/kg of oven dry soil, i.e. rates were increased about eight and sixteen times respectively above those used in the previous experiment.

The treatments were re-randomized every week both between and within replications, to minimize any local environmental effects of position in the glasshouse.

Table 4.1. Amounts of urea applied with added organic matter to bring overall C/N ratio to 12.

O.M. application	Initial C/N of added O.M.	Required C/N of added O.M.	Urea addition (g./kg.) 80 g O.M./kg	160 g.O.M./kg
Without O.M.(Bo, Lo)	0	0	0 (NoBo, NoLo, N1Bo, N1Lo)*	
Barley straw(B1)	104.1	12	6.468 (N1B1)	12.936 (N1B2)
Lucerne chaff(L1)	18.7	12	2.5612 (N1L1)	5.1224 (N1L2)

*The treatments designated N1Bo and N1Lo received no added urea.

4.2.2. Soil and soil preparation

The soil used in this experiment was collected from the A horizon of Burnie clay loam, a krasnozem on the Forthside Vegetable Research Station of the Tasmanian Department of Agriculture. Soil to a depth of 150 mm was collected from

paddock 15. Some physical and chemical properties of this soil have been given in Table 3.1. The soil was selected from the three soils described in Chapter 3 because it was found to contain a high concentration of exchangeable Al together with the lowest level of organic carbon. The preparation of the soil used here has been described in Chapter 2, Section 2.1 (above).

4.2.3. Incubation of soil and soil plus organic matter

The organic materials (barley straw and lucerne chaff) were prepared using the general procedure described in Chapter 2, Section 2.2 and were mixed thoroughly with the soils. The soil plus organic matter mixtures were each spread thinly on a polythene sheet. Half of the required amount of powdered urea (Table 4.1) was sprinkled as evenly as possible over the surface and thoroughly mixed by lifting opposing sides of the sheet in turn and rolling the soil back and forth. The remainder of the urea was then added and the mixing procedure repeated. The urea-treated mixtures were packed uniformly into black polythene pots (diameter,15 cm; height 17.8 cm). Water was added to bring the pot contents approximately to field capacity (pF=2). The mixtures were incubated in the glasshouse (mean temperature 25°C) for a total period of 16 weeks together with untreated soil controls. Water content was maintained by regular weighing and addition of deionized water as required. Polythene food wrap with small holes was used to cover the pots to prevent rapid drying. The pots were sampled after 0, 4, 8, and 16 weeks of incubation. A 25 mm diameter PVC tube was used to withdraw pot contents to full pot depth. The samples were air dried, ground to pass an International 2 mm round-holed sieve and stored in polythene bags at room temperature prior to analysis.

4.2.4. Soil analysis

The methods and details of determination of soil pH, available P, exchangeable Al, and estimation of the ionic strength of the soil solution have been described in Chapter 2, Section 2.5.

4.2.5. Statistical analysis

The data were statistically analysed on an Apple IIe microcomputer using an ANOVA II program (Human Dynamic Systems, Northridge, California, U.S.A.). To compare means, the least significant differences (LSDs) were calculated from the standard errors of the means and the t-value appropriate for the number of degrees of freedom for error.

4.3. Results and Discussion

4.3.1. Soil reaction

The pH of the soils to which barley straw and lucerne chaff had been added was higher than that of the soil without added organic matter over the whole period of incubation, both with and without added urea (Figure 4.1; Appendices 4.1, 4.2). The much higher pH of the N1B1, N1B2, N1L1, and N1L2 treated soils was due to hydrolysis of added urea. The addition of lucerne chaff with and without added urea (NoL1, NoL2, N1L1, and N1L2) was followed by an increase in soil pH somewhat greater than that due to addition of barley straw with and without added urea (NoB1, NoB2, N1B1, and N1B2). These effects may be related to differences in the amounts of organic anions released from the different plant materials and their association with H^+ ions in the soil. The effects of mineralization (and other H^+ consuming or OH^- producing processes, such as ammonia hydrolysis and nitrate reduction by microorganisms) would be likely to be counterbalanced by a concomitant increase in nitrification (Ritchie and Dolling, 1985; and Barrow, 1960).

After the large early increases in pH, the pH differences between the soils with added organic matter and the control soils (without added organic matter) showed little further change. (Figure 4.1). This may be related to the quantity of N available for release during microbial degradation followed by nitrification processes which would tend to cause lower pH values as NO_3-N was formed (Anderegg and Naylor, 1988).

In the organic-matter-plus-urea-treated soil, the pH increased to a much higher level than in the unamended-N soil for all times of incubation. This observation

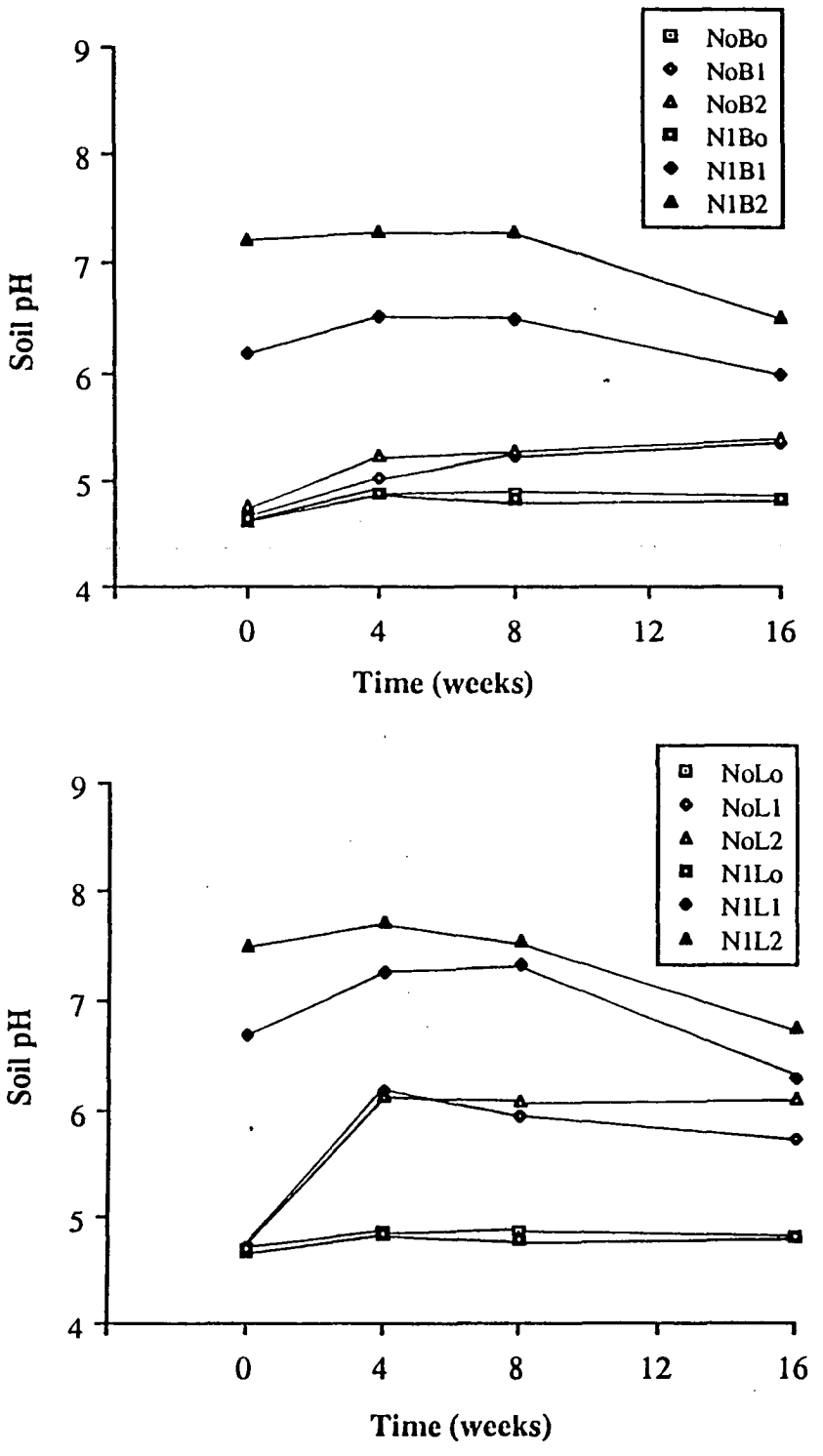


Figure 4.1 The effect of urea-N (No and N1) and organic matter (Barley straw: Bo, B1 and B2, and Lucerne chaff: Lo, L1 and L2) on soil pH with time of incubation. (Treatment NoBo, NoLo, N1Bo and N1Lo are equivalent controls, see Table 4.1)

is in accord with the results reported by Hendrickson et al. (1987) who found substantial N-immobilization and ammonia volatilization in soils following application of urea. Also, Anderegg (1985) found that there was a highly significant positive correlation (r=0.83) between the level of soil NH_4-N and increase in soil pH during short term decomposition of organic matter added to a soil formed on volcanic ash. The urea effect decreased with time, pH values approaching those of the OM-alone treatments at 16 weeks.

4.3.2. Exchangeable aluminium (1 M KCl extractable)

Exchangeable Al was lower in soil incubated with barley straw or lucerne chaff than in untreated control soil for all periods of incubation (Figure 4.2; Appendices 4.3, 4.4). Generally, there were no significant differences between the low and high rates of added organic matter. This effect on soil aluminium (Figure 4.3) could be due to the increases in pH following the addition of organic matter and urea (Figure 4.1). Exchangeable Al decreased rapidly as pH rose above 4.7 to approximately 7.7. Although the effect of lucerne chaff on reducing KCl-extractable Al was greater than that of barley straw in the first four weeks of incubation, this effect was reduced thereafter. This may be due to the low C/N ratio of the lucerne chaff enhancing the activity of soil microorganisms in a shorter time compared with barley straw which, with its higher C/N ratio, required a longer period of incubation time even with the addition of urea.

Decrease in exchangeable Al was most marked over the first four weeks of incubation in the soils that had received added organic matter, both with and without urea, with exchangeable Al falling to less than half of the levels measured at commencement of incubation. Between four and eight weeks of incubation the rate of decrease was much reduced in all soils that had received organic matter and organic matter plus urea. In fact there were small increases in exchangeable Al in the soils receiving lucerne chaff only (NoL1, NoL2). Between 8 and 16 weeks all treated soils except those receiving lucerne chaff only, in which the level of exchangeable Al fell

slightly, showed small increases. It is probably more realistic to interpret the data for the treated soils as indicating little change in the level of exchangeable Al after the first four weeks of incubation. The behaviour of the untreated control soils was different from that of the soils receiving organic matter, with or without urea. The decrease in exchangeable Al between 0 and 4 weeks was much less than for the other soils but continued at the same rate between four and eight weeks by which time the level was about half of that at the start of the experiment. Between 8 and 16 weeks the level of exchangeable Al rose to about the level measured at four weeks. Similar results were obtained by Hoyt and Turner (1975). They also showed that with further incubation (from 16 to 24 weeks), the level of exchangeable Al continued to rise and returned to its original level. The present data are also in accord with the finding of Hue (1988) demonstrating a clear effect of added organic matter in reducing exchangeable Al, which may have been enhanced by addition of urea.

The considerable jump in pH above that of the controls might explain the reduction in exchangeable Al up to four weeks of incubation and there was little change in either parameter thereafter (Figure 4.1, 4.2, 4.3). $Al(OH)_3$ is the preferred form of decreasing solubility in the pH range 4.7 to 7.5 (Magistad, 1925; Pierre et al., 1932; McLean, 1976). However this explanation would not be adequate for the performance of the control soils, because the pH of these soils was virtually constant throughout. It is possible that the initial sharp change in soil wetness and enhanced activity of soil microorganisms in decomposition of native organic matter could have been responsible for the reduced levels of exchangeable Al measured at four and eight weeks. The rise in exchangeable Al between 8 and 16 weeks may perhaps be related to the shortage of substrate for the continued growth of soil microbes and also longer term effects of continued high moisture levels on stability of aluminosilicate clay minerals or aquo-hydroxy polymeric aluminium species.

4.3.3. Available phosphorus (0.5 M $NaHCO_3$ extractable at pH 8.5)

There was a sharp rise in available phosphorus in the first four weeks of incubation of all treated soils in contrast with the controls in which the levels

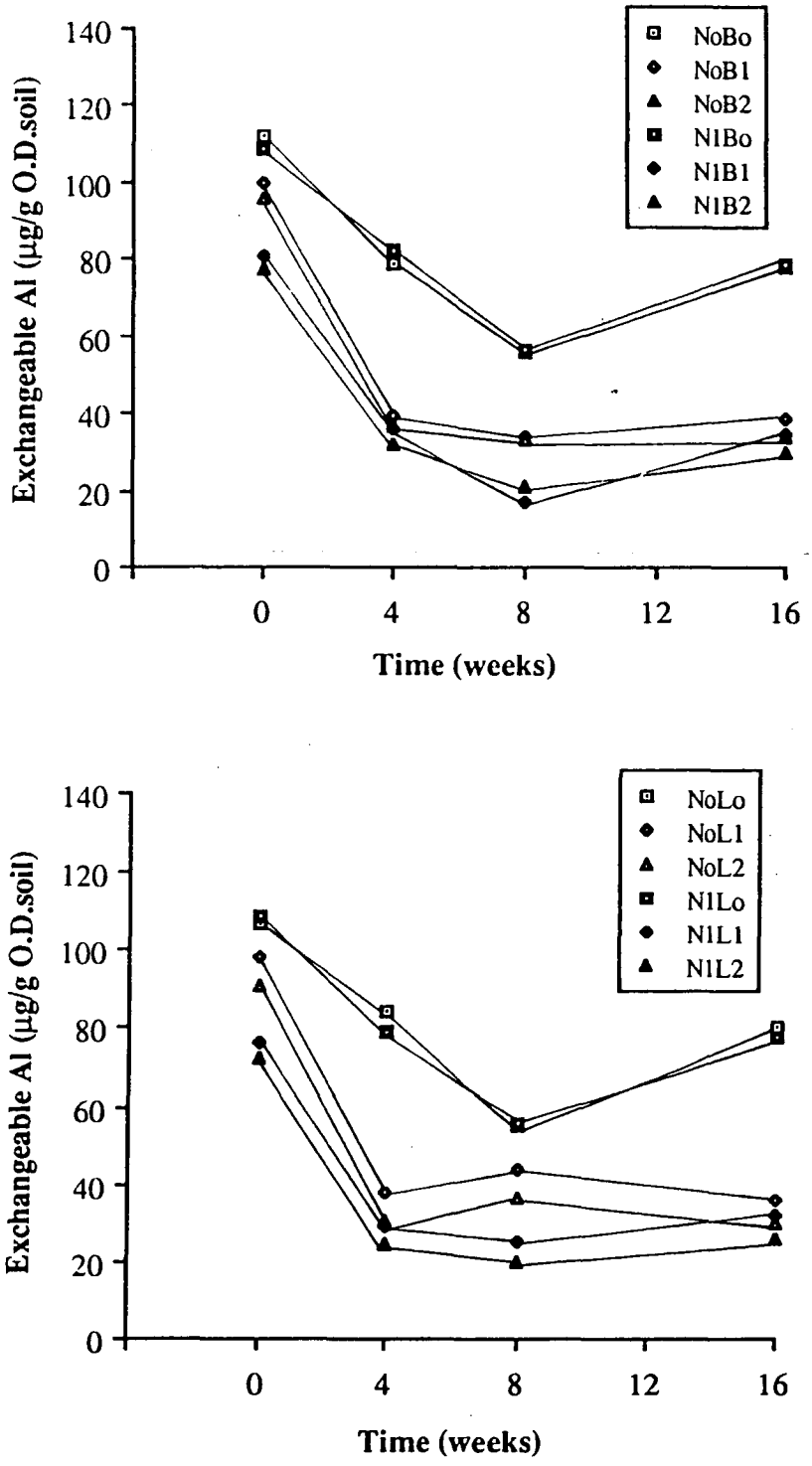


Figure 4.2 The effect of urea-N (No and N1) and organic matter (Barley straw: Bo, B1 and B2, and Lucerne chaff: Lo, L1 and L2) on exchangeable Al with time of incubation. (Treatment NoBo, NoLo, N1Bo and N1Lo are equivalent controls, see Table 4.1)

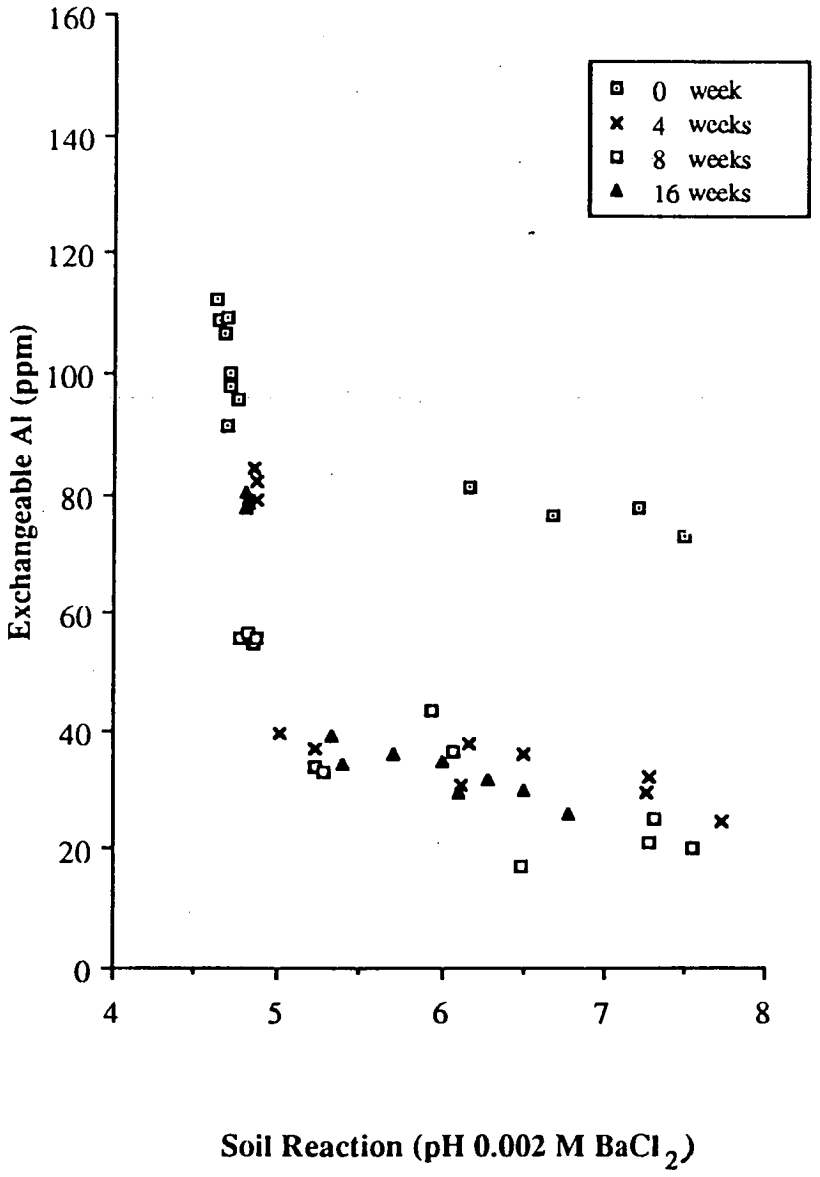


Figure 4.3 Relationship between soil reaction and exchangeable Al in relation to time of incubation.

decreased slightly and continued to decrease at about the same rate throughout the period of incubation (Figure 4.4; Appendices 4.5, 4.6). After four weeks there was an equally rapid fall in the levels of available phosphorus in all treated soils and at the end of the experiment these were well below the levels measured at its commencement.

Generally the levels of available phosphorus were higher in those soils to which both organic matter and urea had been added. There was little difference due to the kind of added organic matter (barley straw vs lucerne chaff) except after 4 weeks of incubation when distinctly higher levels of available phosphorus were maintained in the soils that had received lucerne chaff. This could be due to the interaction between urea and organic matter during decomposition which directly affected pH and exchangeable aluminium as discussed above. Futhermore, the levels of available phosphorus were at all times higher than in the controls, with one exception i.e., the 16 week value for the soil receiving the lower level of lucerne chaff without urea (NoL1).

Nevertheless, the effect of added organic matter and organic matter plus urea on available phosphorus was short-lived, with levels falling below those at the commencement of the experiment by 16 weeks. This may be explained as due to an increase in microbiological activity stimulated by addition of organic matter, with the production of low-molecular-weight organic anions capable of displacing orthophosphate anions and/or occluding phosphorus sorption sites (Nagarajah et al., 1970), thus freeing it for bicarbonate extraction. The enhancement of this process by urea could explain the somewhat higher levels of available phosphorus measured for the organic-matter-plus-urea-treated soils. It should be noted that the reduced levels of available phosphorus after four weeks were not paralelled by increases in extractable Al which changed little in the organic-matter-treated soils. Thus it seems likely that labile phosphorus was utilized by microorganisms so that there was less available for extraction by 0.5 M $NaHCO_3$.

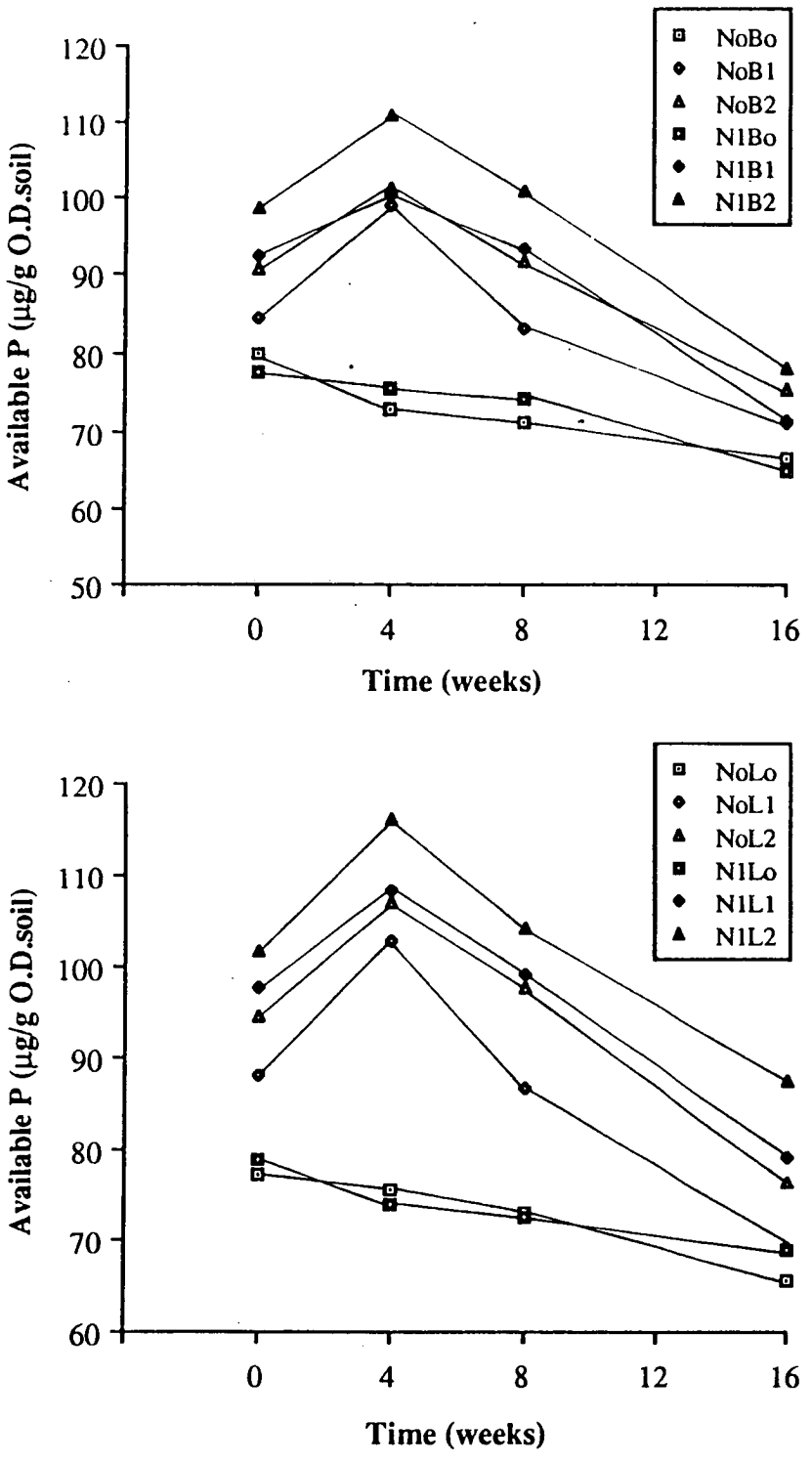


Figure 4.4 Effect of urea-N (No and N1) and organic matter (Barley straw: Bo, B1 and B2, and Lucerne chaff: Lo, L1 and L2) on available P in relation to time of incubation. (Treatment NoBo, NoLo, N1Bo and N1Lo are equivalent controls, see Table 4.1)

4.3.4. Ionic strength of soil solution (I.S.)

The application of organic matter had a great influence on increasing I.S. of soil solution in soils treated with barley straw or lucerne chaff (Figure 4.5 and Appendices 4.7,and 4.8). Levels of soil solution I.S. rose sharply from 0 to 4 weeks after which levels were maintained. The control soils showed little or no change in soil solution I.S. throughout the experiment. There was a markedly greater increase in soil solution I.S at each level of added organic matter after addition of lucerne chaff compared with barley straw. In both cases added urea enhanced the main effect of organic matter. Since large increases in I.S. would be expected to lower pH while quite large increases in pH were measured, it is clear that there were competing mechanisms in play.

It is well known that organic matter influences the point of zero charge in soils of variable charge and thus the cation exchange capacity (CEC) and anion exchange capacity (AEC); eg. El-Swaify and Sayegh, 1975; Gillman and Bell, 1976; and Gillman, 1985. The increased effects of added organic matter in the presence of urea in this experiment may again be due to stimulation of microorganism activity. Equally this may be the explanation for the greater effects of lucerne chaff with its lower C/N ratio and more rapid rate of decomposition compared with barley straw. There were only small differences attributable to rate of applied organic matter and for practical purposes the lower rate (80 g/kg) should be sufficient both to improve the level of available phosphorus for crops in the short to medium term and to reduce the level of exchangeable aluminium. The greater amount of urea added with the higher level of organic matter (160 g/kg) resulted in a considerably higher I.S.. Its effects on exchangeable aluminium and phosphorus have been discussed earlier.

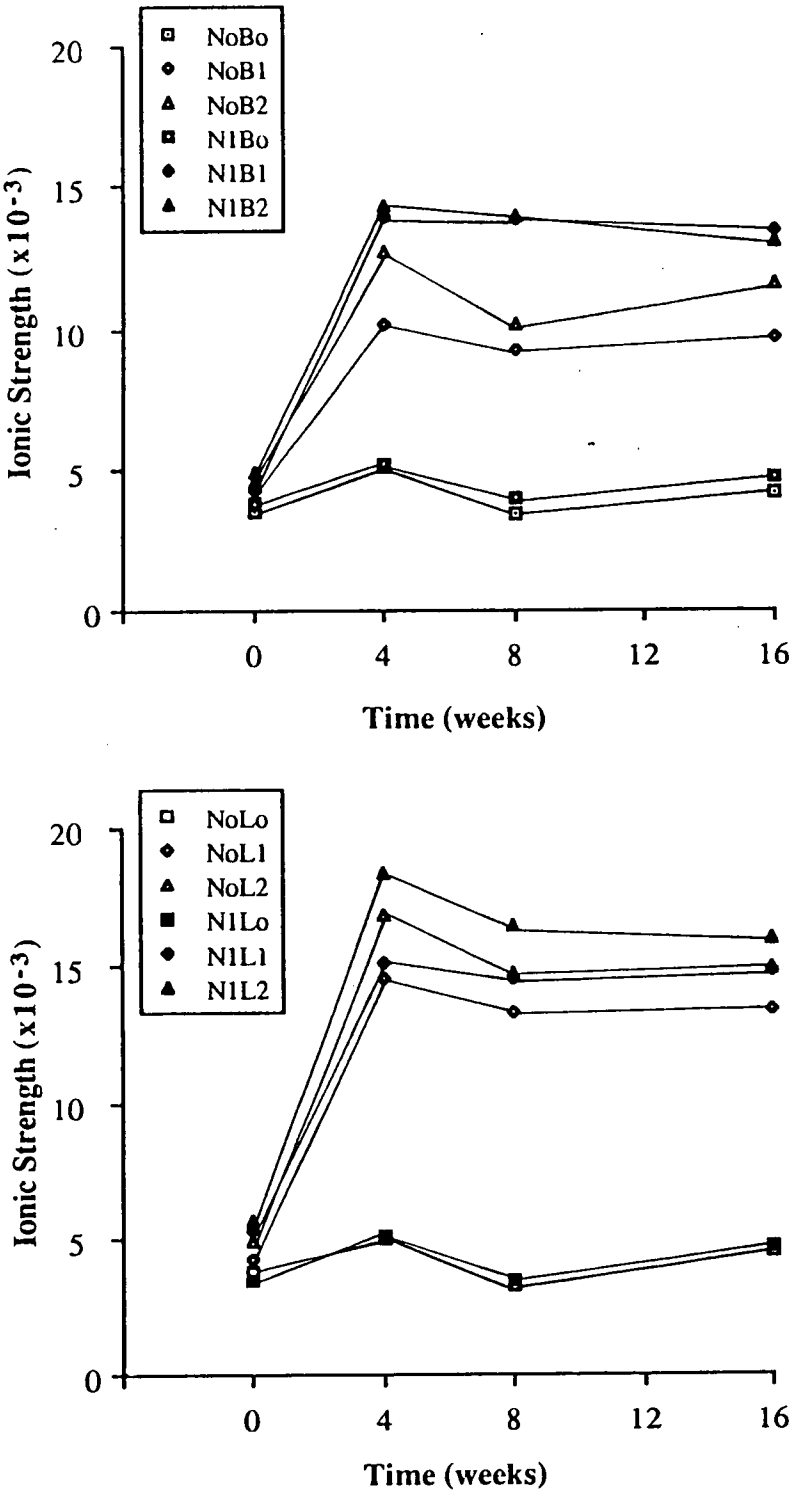


Figure 4.5 Effect of urea-N (No and N1) and organic matter (Barley straw: Bo, B1 and B2, and Lucerne chaff: Lo, L1 and L2) on ionic strength of soil solution in realation to time of incubation. (Treatment NoBo, NoLo, N1Bo and N1Lo are equivalent controls, see Table 4.1)

5. SOME EFFECTS OF ORGANIC MATTER ON THE LEVEL OF ACTIVE ALUMINIUM IN SOIL IN RELATION TO AVAILABLE PHOSPHORUS AND PLANT GROWTH

5.1. Introduction

It is known that organic matter is capable of reducing the severity of aluminium toxicity in acid soils. However, its effectiveness on soil phosphorus and improving plant growth under conditions of aluminium stress is still doubtful. The chelation or complexing activity of organic matter with aluminium has been correlated with the position and number of hydroxyl and carboxyl groups (Hue et al., 1986). In the early stages of decomposition, it is well known that most organic materials produce mainly organic acids and that these play an important role in reducing the level of aluminium in the soil solution. The effectiveness of organic matter in forming chelation or other complexes with aluminium should depend on its stage of decomposition. From the results of the previous experiment (Chapter 4), it was concluded that organic matter added to Burnie clay loam A horizon was most effective in reducing the level of exchangeable aluminium after incubation for one to two months.

Therefore a second experiment was conducted to investigate further the effectiveness of added organic matter in reducing levels of active aluminium in relation to available phosphorus levels and plant growth response. In this experiment soluble aluminium was added:

(a) after incubation of soil plus organic matter for one month, and

(b) at the same time as organic matter.

The test plant used was perennial ryegrass (Lolium perenne L.).

5.2. Materials and Methods

5.2.1. Experimental design

The variables in this experiment were:

Variable (1): two types of organic matter, viz., chopped barley straw and lucerne chaff;

Variable (2): two rates of organic matter, viz., nil organic matter and added organic matter at 80 g/kg of soil (O.D.) i.e. 96 g/pot;

Variable (3): four rates of aluminium as hydrated aluminium sulphate [$Al_2(SO_4)_3 \cdot 14H_2O$], viz., 0, 25, 50, and 100 µg Al/g soil:

Treatment	Al application rate µg/g soil	mg/pot	$Al_2(SO_4)_3 \cdot 14H_2O$ g/pot
Ao	0	0	0
A1	25	30	0.3303
A2	50	60	0.6606
A3	100	120	1.3212

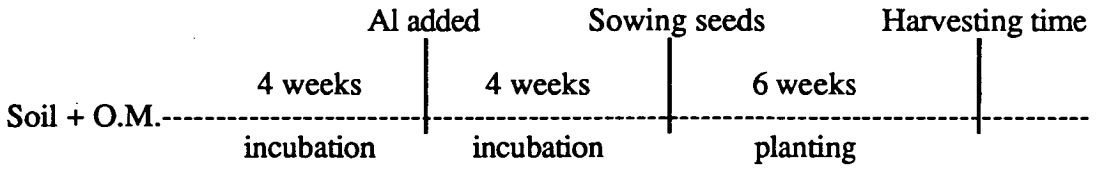
The treatments were applied in a split-split plot design with three replications, aluminium sulphate being mixed with pot contents:

Sequence (a), after incubation of soil with and without organic matter at field capacity for four weeks followed by incubation for a further four weeks before sowing of seed of the test plant, and

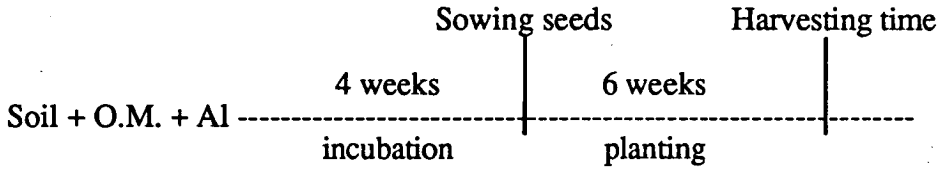
Sequence (b), together with organic matter followed by incubation coincident with the second month of incubation of the sequence (a) pots, with simultaneous sowing of seed of the test plant in all pots.

The sequence of operations was:

Sequence (a):



Sequence (b):



5.2 2. Soil and organic materials

The soil used was the surface 15 cm (A horizon) of Burnie clay loam as in the previous experiment (Table 3.1). The Burnie clay loam soil was selected for this experiment because of its low pH and relatively high level of available phosphorus.

The same two kinds of organic matter were used, barley straw and lucerne chaff, as in the first experiment and prepared as before. For this experiment, basal nutrients were applied in powder form before sowing at rates (g/kg soil): KNO_3, 1.36; $MgSO_4.7H_2O$, 0.192; $CaCO_3$, 4.24. One week after sowing, 0.1% (w/v) ammonium molybdate solution was sprayed onto the soil surface and this was repeated weekly thereafter.

5.2.3. Incubation of soil and soil plus organic matter mixtures and addition of aluminium

Sequence (a): 1.2 kg (O.D.) lots of soil and soil thoroughly mixed with 80 g/kg of either chopped barley straw or lucerne chaff were placed in 150 mm diameter black polythene pots. Deionized water was added with weighing to bring the pot contents to field capacity. The pots were covered with polythene food wrap with small holes pricked through it to prevent excessive surface drying. Any water loss

was made good daily by adding water to restore initial weight. The pot contents were incubated in this condition in the glasshouse for four weeks.

After four weeks the pot contents were emptied onto polythene sheets and spread thinly. Half of the required amount of aluminium per pot, as powdered hydrated aluminium sulphate, was sprinkled evenly over the pot contents followed by uniform, thorough mixing by lifting opposite edges of the polythene sheet and rolling the mixtures back and forth. The remaining half of the required amount of aluminium sulphate was then added and mixed in the same way. The mixtures were then re-packed into the pots (bulk density, 0.89) and incubated as described above for a further four weeks.

Sequence (b): Aluminium sulphate was added in the same way to other 1.2 kg lots of soil and soil plus organic matter which had not been subjected to the first four weeks of incubation. These mixtures were packed into pots and incubated for four weeks together with the sequence (a) pots. Thus, before sowing of the test plant, sequence (a) pots were incubated for eight weeks (four weeks before and four weeks after addition of aluminium sulphate) and
sequence (b) pots were incubated for four weeks only after addition of aluminium sulphate.

5.2.4. Plant growth, harvest and preparation of plant material for analysis

Seed of " nui " cultivar perennial ryegrass (Lolium perenne L.) supplied by the Department of Agriculture, Tasmania, was sown at 1 cm depth at the rate of 20 seeds per pot. Prior to sowing, seed was soaked and aerated overnight in deionized water to enhance germination. The plants were thinned at early seedling stage (2 cm) to 8 plants per pot. No artificial lighting was used. Temperature was maintained at about 25 ^{o}C during the day and not less than 10 ^{o}C at night.

All pots were moistened with deionized water to estimated field capacity (pF 2) and this was maintained by daily weighing and addition of water.

Treatment locations were fully randomized at the outset and re-randomized each week until harvest.

Plant tops were harvested after 6 weeks growth by cutting off with scissors just above soil level. Any soil contamination of the lower stems was removed immediately by a quick rinse with deionized water followed by blotting dry with white tissue. Plant material was placed in brown paper bags and dried for 48 hours in a forced draught oven at 65 °C. Remaining stems and roots were separated from soil using a 2 mm. sieve. Small roots and root fragments passing through the screen were collected and included with the root samples. The separated roots were cleaned thoroughly under a stream of tap water before rinsing in deionized water and oven drying as with plant tops.

The dried plant materials were cooled to room temperature in a desiccator and weighed. The larger samples were ground in a "Culatti" hammer-mill while smaller samples were ground by hand in a glass mortar to avoid any loss of tissue. Each finely ground sample was thoroughly mixed and stored in a glass vial. Immediately before chemical analysis, the ground samples were redried at 65 °C and cooled in a desiccator.

5.2.5. Chemical analysis of plant materials

Perchloric-nitric digestion: subsamples of plant material were digested in a 1:5 (v/v) mixture of perchloric and nitric acids. The method was adapted from that described by Huett (1979) and by Zasoski and Burau (1977). The modified procedure was:

(1) exactly 100 mg subsamples of oven-dried, ground plant material were placed in "Pyrex" test tubes (diam., 1.8 cm) marked for a final liquid volume of 20 ml;

(2) 5 ml. conc. HNO_3 (71.0%, w/w) was added and the samples were left to pre-digest overnight at room temperature in order to minimize subsequent frothing;

(3) the test tubes and contents were then placed in the sockets of an aluminium heating block on a thermostatically controlled electric hot plate, the temperature was raised gradually to approximately 110 °C, and the samples were digested for approximately one hour or until no particulate organic matter remained; if too vigorous frothing occurred during this stage of the digestion the tubes were lifted from the heating block and allowed to cool briefly until frothing subsided before being returned to the block;

(4) the samples were then cooled briefly before addition of 1 ml conc. $HClO_4$ (70%, w/w);

(5) after addition of perchloric acid the tubes and contents were returned to the heating block, the temperature was raised gradually to 180-200 °C and the digestion was continued for a further 2-3 hours or until there was no further evolution of dense, white fumes and the digestate was colourless;

(6) the digestate was allowed to cool briefly and diluted with deionized water to the 20 ml mark while still warm (to avoid the formation of potassium perchlorate crystals);

(7) the tubes were then placed in a vortex mixer, the contents were thoroughly mixed and silica was allowed to settle before subsamples of digestate were withdrawn for analysis.

Phosphorus: Phosphorus was determined in 5 ml aliquots of the digestate using the method of Jackson (1958). 10 ml of vanadomolybdate reagent was added to each 5 ml aliquot in 50 ml volumetric flasks; the mixture diluted to 50 ml with deionized water and mixed thoroughly. After 30 minutes colour development optical density was measured at 440 nm in a Bauch and Lomb Spectronic 20 spectrophotometer. Phosphorus was determined from a standard curve in the range 0-10 $\mu gP\ ml^{-1}$.

5.2.6. Chemical analysis of soil materials

The pot contents were sampled after harvest of plant materials and the specimens were air dried in the glasshouse. The air-dried materials were ground to pass a 2 mm. round-holed sieve and stored in polythene bags.

Soil Reaction (pH): This was determined in a 1:5, soil : 0.002 M $BaCl_2$ suspension (Gillman and Sumpter, 1986).

Ionic strength of soil solution at field capacity: This was estimated by the method of Gillman and Bell (1978). the data were subjected to multiplication transformation using a computer programme (ANOVA II, Version 1.1, Human Systems Dynamics, 1983) prior to analysis of variance using the same computer programme.

Exchangeable Aluminium: Aluminium in a 1 M KCl extract (Barnhisel and Bertsch, 1982) was determined by the aluminon method (Hsu, 1963). Ascorbic acid was used to eliminate iron interference (Jayman and Sivasubramaniam, 1974).

Available Phosphorus: This was extracted by shaking with 0.5 M $NaHCO_3$ at pH 8.5 for 16 hours at room temperature, 25±1 ^oC (Olsen and Sommers, 1982). Phosphorus was determined in the extract by the colorimetric method of Murphy and Riley (1962).

5.2.7. Soil solution extraction and analysis

(a) Soil solution extraction: Soil solution was extracted directly from the moist soil (approximately pF2, or field capacity) after harvest of plant material by the centrifuge method described by Gillman (1976). Gillman's apparatus was modified to fit the 50 ml cups of an MSE Magnum centrifuge. The assembly is shown in Figure 5.1.

The assembly was made from 100 ml polycarbonate contrifuge tubes. The three parts of the assembly were firmly joined by Scotch tape. The capacity of the soil-containing section was approximately 30 gm of moist soil (pF2). Eight assemblies were contrifuged in each batch at 2000 rpm for 15 minutes. The expressed

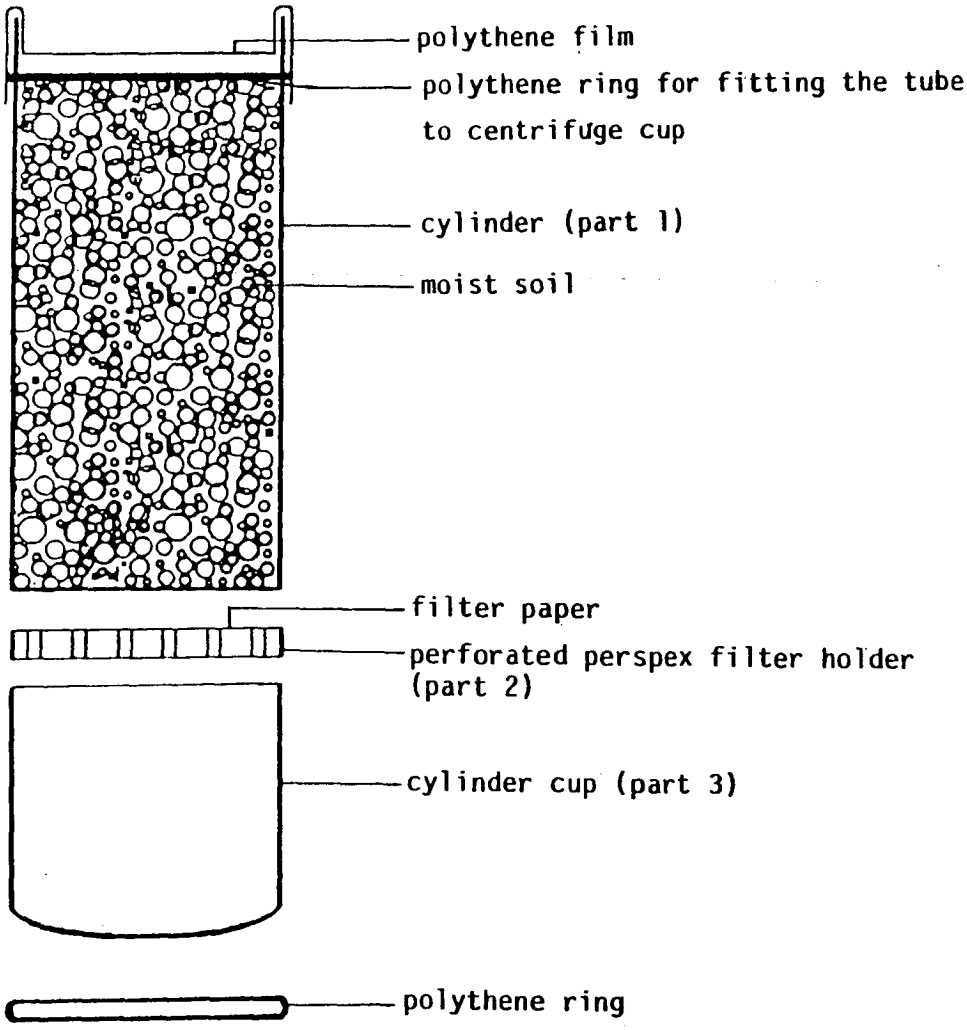


Figure 5.1 Centrifuge tube device for extraction of soil solution

soil solution passed through a 0.22 μm Millipore filter into the lower cylinder cup. The clear soil solution extracts were stored in the refrigerator to reduce the growth of microorganisms if subsequent analysis could not be carried out within the same day.

(b) **Soil solution analysis:**

Phosphorus: Phosphorus was determined directly using the method of Murphy and Riley (1962).

Aluminium: Inorganic monomeric and organically complexed forms of aluminium were determined using a new short-term colorimetric method (Kerven and Edwards, 1987). Pyrocatechol violet (PCV) was used as a chromogenic reagent to measure monomeric aluminium in the concentration range 0.2-25 μM. The different reaction rates between PCV and aluminium in monomeric versus organically complexed forms provided a means of discrimination between them.

Two calibration curves were required. The first was a standard curve for aluminium in the range 0-25 μM using aluminium nitrate [$Al(NO_3)_3 \cdot 9H_2O$] standards and a colour development time of 20 minutes. The second curve was prepared using standards containing different ratios of two forms of aluminium viz., as aluminium nitrate and aluminium malate. The latter salt was used instead of aluminium fulvate because its reaction is similar to that of aluminium fulvate and it is easier to prepare (Kerven personal comm.). The amount of aluminium that reacted with PCV in 60 seconds was determined from absorbance at a wavelength of 585 nm measured by a Beckman DU-30 spectrophotometer fitted with a sample sipper. The calibration curve was prepared by plotting fraction of total aluminium in inorganic.form versus fraction of total aluminium reacted.

Total aluminium in soil solution extracts was measured by ICPES (Inductively Coupled Plasma Emission Spectroscopy). These data and those from the fraction of aluminium reacted in 60 seconds made it possible to calculate the concentrations of monomeric inorganic aluminium and organically complexed aluminium.

5.3. Results and Discussion

5.3.1. Sequence (a)

Aluminium: Exchangeable aluminium increased ($P<0.001$) with addition of aluminium as $Al_2(SO_4)_3 \cdot 14H_2O$ (Figure 5.2; Appendix 5.1).

The effect of added organic matter was seen in a much lower level ($P<0.001$) of exchangeable aluminium than in the soils without added organic matter at each level of aluminium application. The effect of lucerne chaff was greater ($P<0.05$) than that of barley straw (Table 5.1).

Evans and Kamprath (1970) and Hoyt and Turner (1975) considered that declining aluminium toxicity in their soils was due primarily to complexing of exchangeable aluminium by organic matter. Generally, the phytotoxic forms of aluminium are known to include the monomeric species; $AlOH^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$, $Al(OH)_4^{-}$, and $Al(OH)_5^{2-}$ (Blamey et al., 1983).

Monomeric aluminium in the soil solution also increased markedly ($P<0.001$) with increasing aluminium application (Figure 5.3, Table 5.2, Appendix 5.1). These increases were much lower ($P<0.001$) in the presence of added organic matter while the level of organically complexed aluminium increased ($P<0.001$)(Figure 5.4). There was little change in organically complexed aluminium in the absence of added organic matter. Thus following addition of organic matter much of the soil solution aluminium was present in the form of Al-organic complexes which are not toxic to plants (Bartlett and Riego, 1972; and Hue et al., 1986).

The levels of total aluminium and organically complexed aluminium in the soil solution were higher ($P<0.01$ and $P<0.001$) when organic matter was added as barley straw than when it was added as lucerne chaff (Figure 5.4 a, b; Table 5.3, 5.4; Appendix 5.2). This may be due to the different composition of the plant materials themselves together with the somewhat higher pH of the soil plus lucerne chaff plus aluminium media. Although the differences in the effects of barley straw and lucerne chaff on monomeric Al in the soil solution were not significant ($P>0.05$), there was an increasing divergence with rate of aluminium application of the curves for

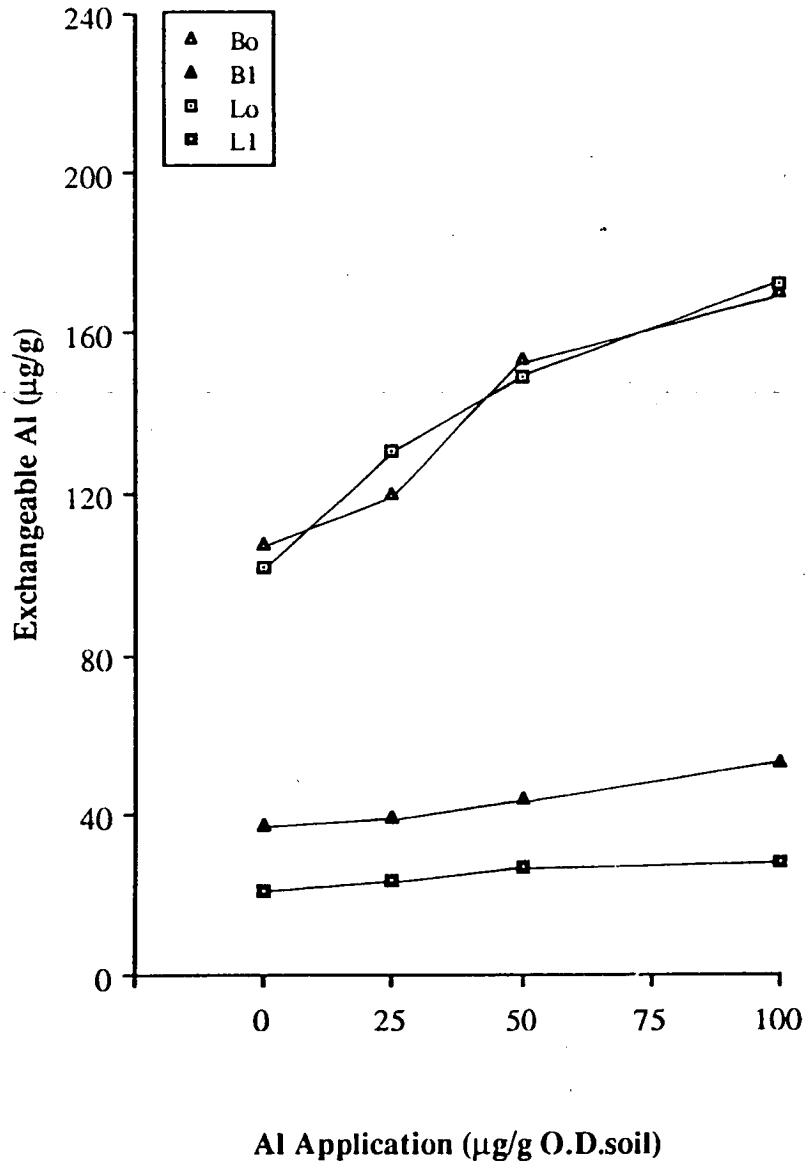


Figure 5.2 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and exchangeable aluminium (1 M KCl) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.1 Exchangeable Al in relation to type of organic matter, rate of organic matter and level of Al application (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	72.59	79.69	98.76	112.02	90.76
Lucerne chaff	61.39	77.07	87.77	100.43	81.66
mean					
(A)	66.99	78.38	93.26	106.22	

LSD (0.05); O.M. type (T) = 7.02 * T x A = NS
Al application (A) = 12.72 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	104.95	125.53	151.36	171.63	138.37
With O.M.	29.02	31.22	35.17	40.81	34.06

LSD (0.05); O.M. rate (R) = 7.91 *** R x A = 23.58 *

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	138.19	43.34	90.76
Lucerne chaff	138.55	24.78	81.66

LSD (0.05); T x R = 11.2 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	107.9	120.3	153.9	170.8	37.3	39.1	43.6	53.3
Lucerne chaff	102.0	130.8	148.9	172.5	20.7	23.3	26.7	28.3

LSD (0.05); T x R x A = NS

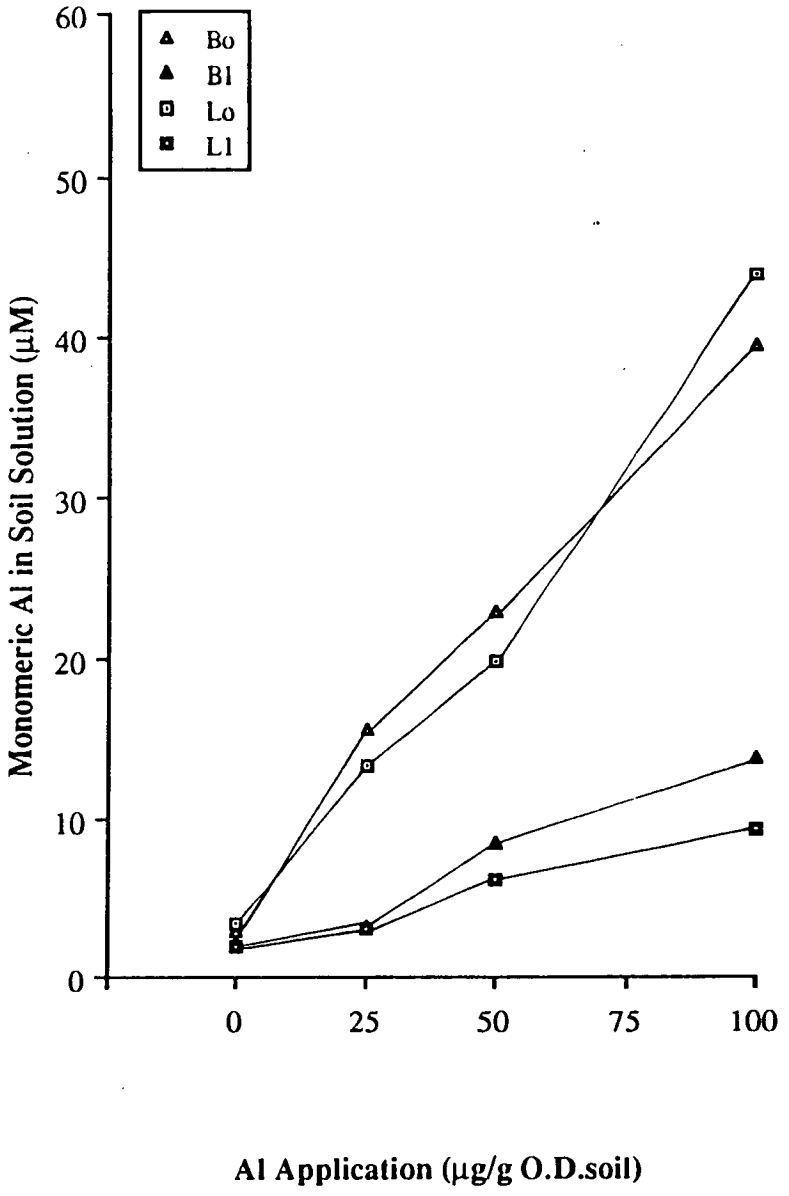


Figure 5.3 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and concentration of monomeric aluminium in soil solution with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.2 Concentration of monomeric Al in soil solution in relation to type and rate of organic matter and level of Al application (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	2.57	9.43	15.63	26.6	13.55
Lucerne chaff	2.69	8.18	12.98	26.62	12.61
mean (A)	2.63	8.8	14.3	26.61	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 3.91 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	3.17	14.37	21.3	41.75	20.15
With O.M.	2.07	3.23	7.3	11.46	6.02

LSD (0.05); O.M. rate (R) = 2.83 *** R x A = 7.95 ***

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	20.21	6.90	13.55
Lucerne chaff	20.09	5.14	12.61

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	2.98	15.50	22.82	39.53	2.15	3.35	8.44	13.66
Lucerne chaff	3.37	13.24	19.78	43.97	2.00	3.12	6.17	9.27

LSD (0.05); T x R x A = NS

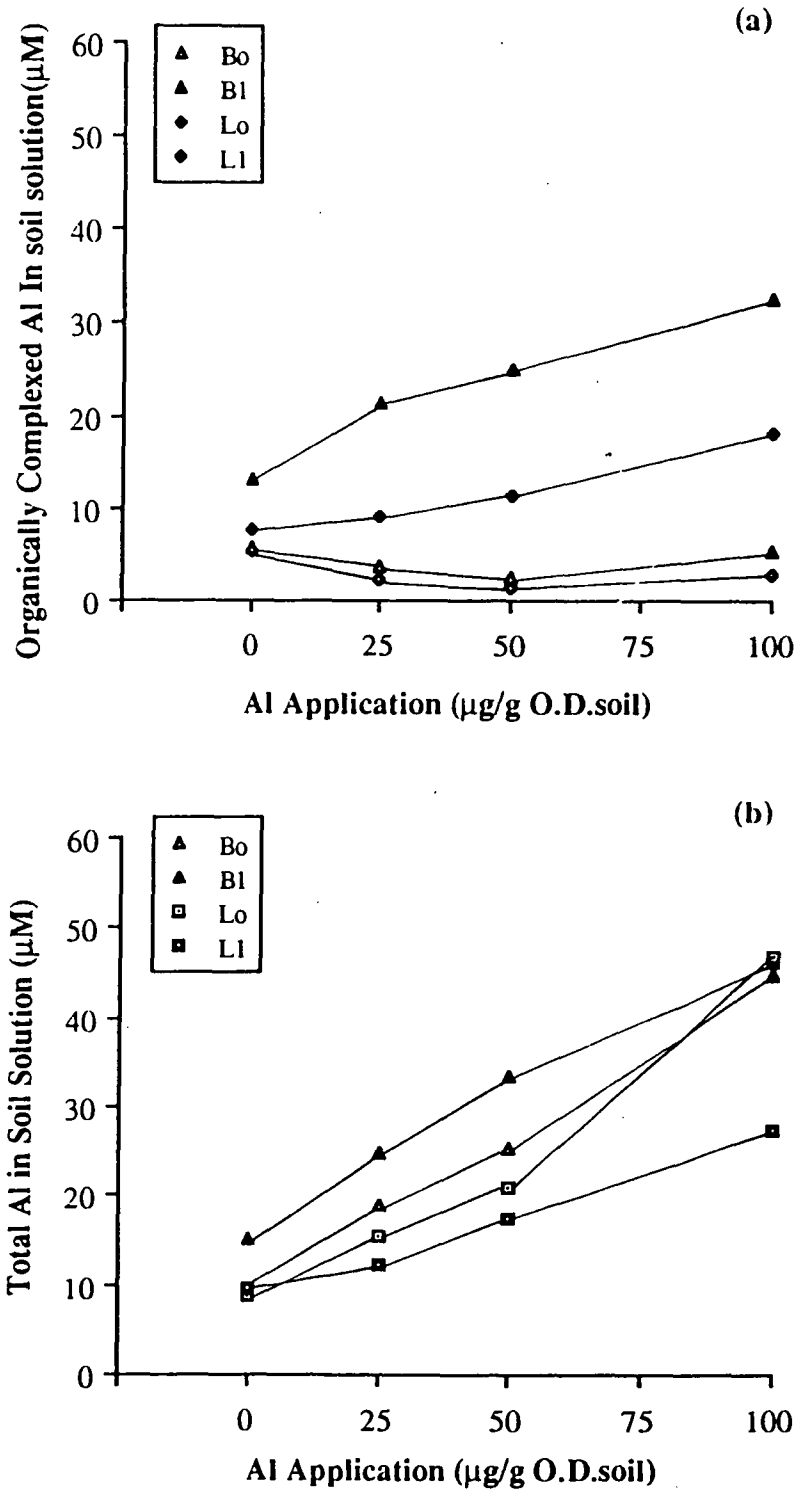


Figure 5.4 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and organically complexed aluminium (a) and total aluminium (b) in soil solution with and without added organic matter as barley straw(B1, Bo) or lucerne chaff (L1, Lo).

Table 5.3 Concentration of organically complexed Al in soil solution in relation to type and rate of organic matter and level of Al application (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	9.32	12.51	13.84	19.10	13.69
Lucerne chaff	6.54	5.74	6.28	10.43	7.25
mean (A)	7.93	9.12	10.06	14.76	

LSD (0.05); O.M. type (T) = 1.91 *** T x A = NS
Al application (A) = 2.85 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	5.51	2.91	1.92	4.10	3.61
With O.M.	10.34	15.33	18.20	25.43	17.33

LSD (0.05); O.M. rate (R) = 2.48 *** R x A = 5.37 **

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	4.29	23.10	13.69
Lucerne chaff	2.94	11.56	7.25

LSD (0.05); T x R = 3.51 **

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	5.64	3.56	2.53	5.43	13.00	21.45	25.16	32.77
Lucerne chaff	5.38	2.27	1.32	2.78	7.69	9.21	11.24	18.09

LSD (0.05); T x R x A = NS

Table 5.4 Concentration of total Al in soil solution in relation to type and rate of organic matter and level of Al application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	11.89	21.93	29.48	45.7	27.25
Lucerne chaff	9.23	13.92	19.26	37.06	19.86
mean (A)	10.56	17.92	24.37	41.38	

LSD (0.05); O.M. type (T) = 3.75 ** T x A = NS
Al application (A) = 2.73 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	8.68	17.28	23.22	45.85	23.76
With O.M.	12.42	18.56	25.5	36.89	23.35

LSD (0.05); O.M. rate (R) = NS R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	24.50	30.00	27.25
Lucerne chaff	23.03	16.70	19.86

LSD (0.05); T x R = 2.81 **

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	8.62	19.06	25.35	44.96	15.15	24.80	33.60	46.43
Lucerne chaff	8.75	15.51	21.10	46.75	9.70	12.33	17.41	27.36

LSD (0.05); T x R x A = NS

monomeric aluminium, the higher levels being associated with barley straw (Figure 5.3; Table 5.2).

The activity of monomeric aluminium is considerably influenced by ionic strength (Blamey et al., 1983; Alva et al., 1986; Kim et al., 1987). Kim et al. (1987) stated that more than 98% of total aluminium was present as monomeric species in very low ionic strength nutrient solutions. The failure of other workers to obtain similar results may be due to their use of higher ionic strength nutrient solutions (Munns, 1965; Osborne et al., 1981; and Bouma et al., 1981).

It is evident that soil solution ionic strength estimated from electrical conductivity of a 1:5 soil extract (Gillman and Bell, 1978) increased with level of aluminium application ($P<0.001$) (Figure 5.5; Table 5.5; Appendix 5.3). Ionic strength was much higher following addition of organic matter ($P<0.05$) but there was no difference due to kind of organic matter ($P>0.05$). The effect of added aluminium on increasing ionic strength may be due to the displacement of other cations (e.g. Ca, Mg, K, Na) from exchange sites into the soil solution. In general, aluminium is held tightly in comparison with other cations, so that increasing levels of soluble aluminium should result in increased displacement of other cations from exchange sites. This effect has been noted by Nye et al. (1961) who found no aluminium in the soil solution until aluminium saturation of the total cation exchange capacity exceeded 60 per cent. The much higher ionic strength after addition of organic matter might be associated with the role of mineralisation of organic matter addition and a consequence of retention of aluminium in the solution phase as complexes or chelates reducing its activity in displacement of other cations from exchange sites, while added organic matter may also contribute to an increased cation exchange capacity (Gillman, 1985).

Soil reaction: The pH of soil both with and without added organic matter decreased ($P<0.05$) with increasing level of added aluminium (Figure 5.6; Table 5.6; Appendix 5.3) and exchangeable aluminium and monomeric aluminium in the soil solution increased rapidly to high values as pH fell below 4.8 (Figure 5.7).

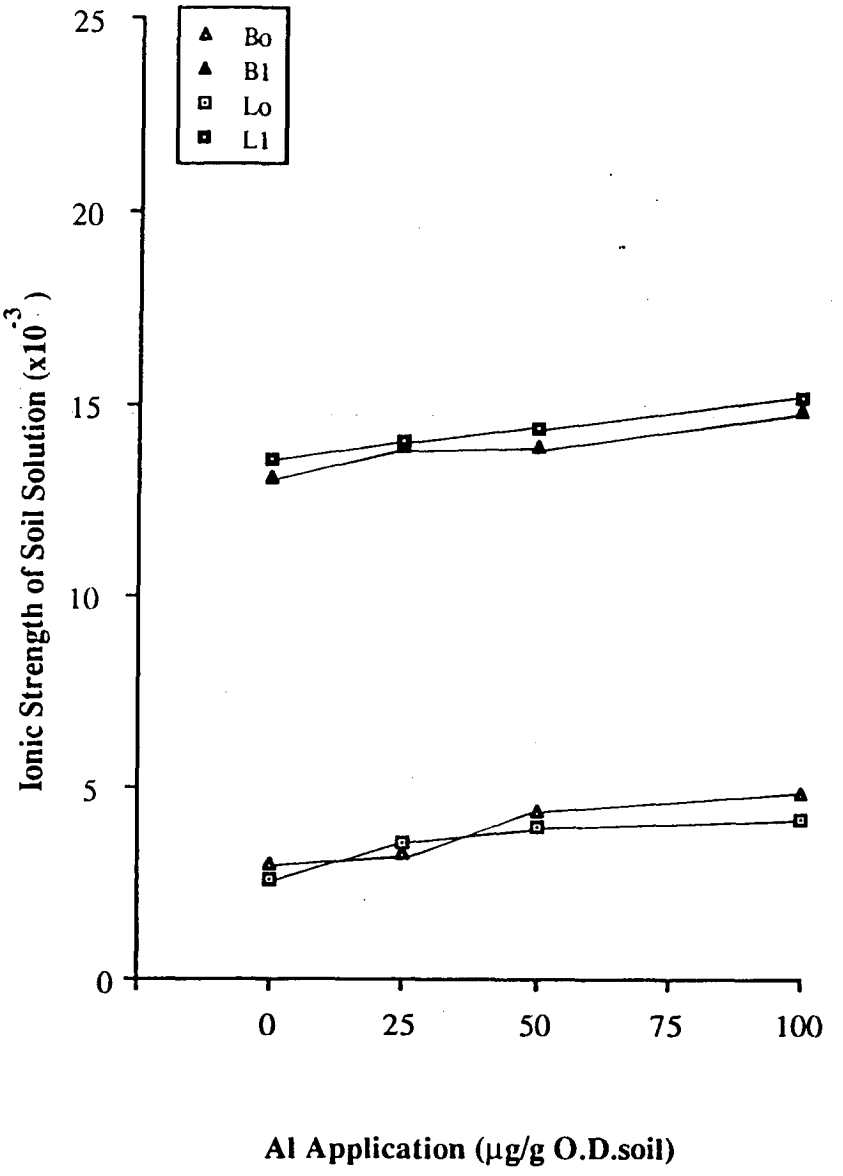


Figure 5.5 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and ionic strength of soil solution with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.5 Ionic strength of soil solution in relation to type of organic matter, rate of organic matter and level of Al application (Mean of three replicates $\times 10^{-3}$)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	8.02	8.58	9.11	9.86	8.89
Lucerne chaff	8.07	8.81	9.17	9.68	8.93
mean (A)	8.04	8.69	9.14	9.77	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.54 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	2.8	3.42	4.16	4.5	3.72
With O.M.	13.29	13.96	14.12	15.04	14.10

LSD (0.05); O.M. rate (R) = 0.33 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	3.86	13.92	8.89
Lucerne chaff	3.58	14.29	8.93

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	2.98	3.28	4.34	4.85	13.06	13.88	13.89	14.87
Lucerne chaff	2.62	3.56	3.98	4.15	13.53	14.05	14.36	15.21

LSD (0.05); T x R x A = NS

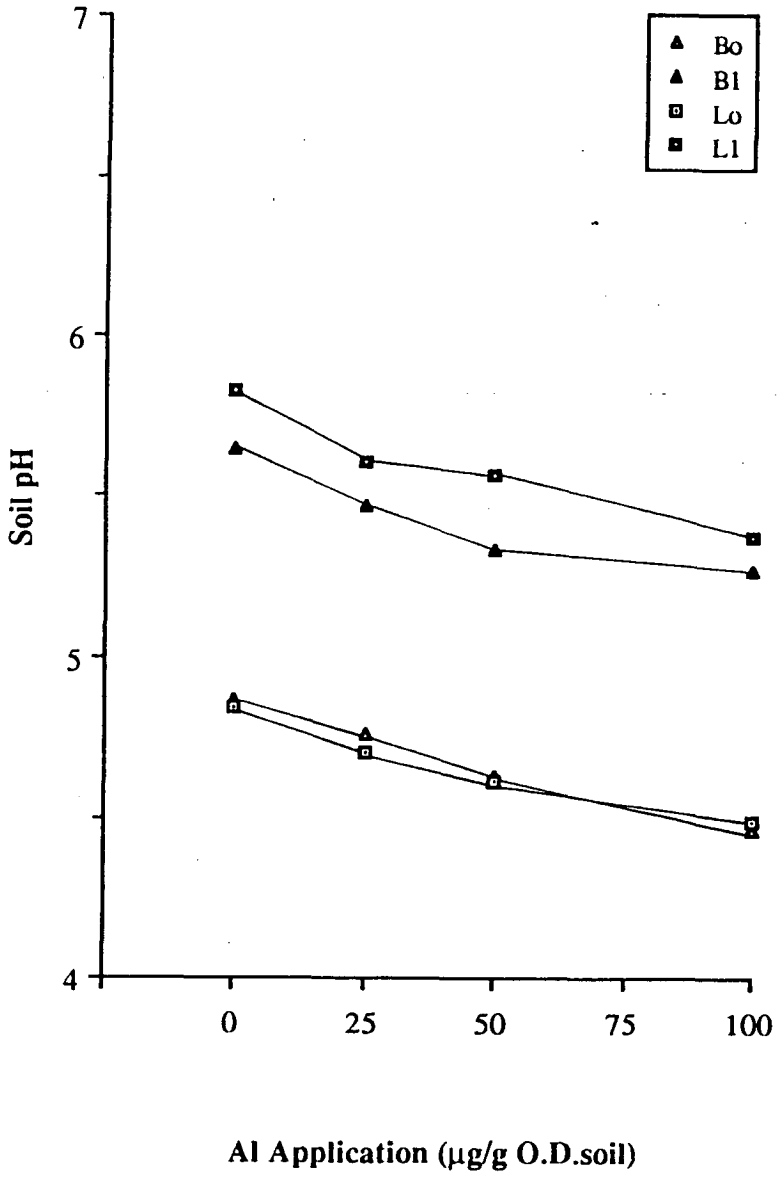


Figure 5.6 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and soil pH with and without added organic matter as barley straw (Bl, Bo) or lucerne chaff (Ll, Lo).

Table 5.6 Effect on soil pH of type and rate of added organic matter and level of Al application. (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	5.26	5.12	4.98	4.87	5.05
Lucerne chaff	5.34	5.15	5.09	4.93	5.13
mean (A)	5.30	5.13	5.03	4.90	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.228 *

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	4.85	4.73	4.62	4.48	4.67
With O.M.	5.74	5.54	5.45	5.32	5.51

LSD (0.05); O.M. rate (R) = 0.341 ** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	4.68	5.43	5.05
Lucerne chaff	4.66	5.60	5.13

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	4.87	4.76	4.63	4.47	5.65	5.47	5.33	5.27
Lucerne chaff	4.84	4.70	4.61	4.49	5.83	5.61	5.57	5.37

LSD (0.05); T x R x A = NS

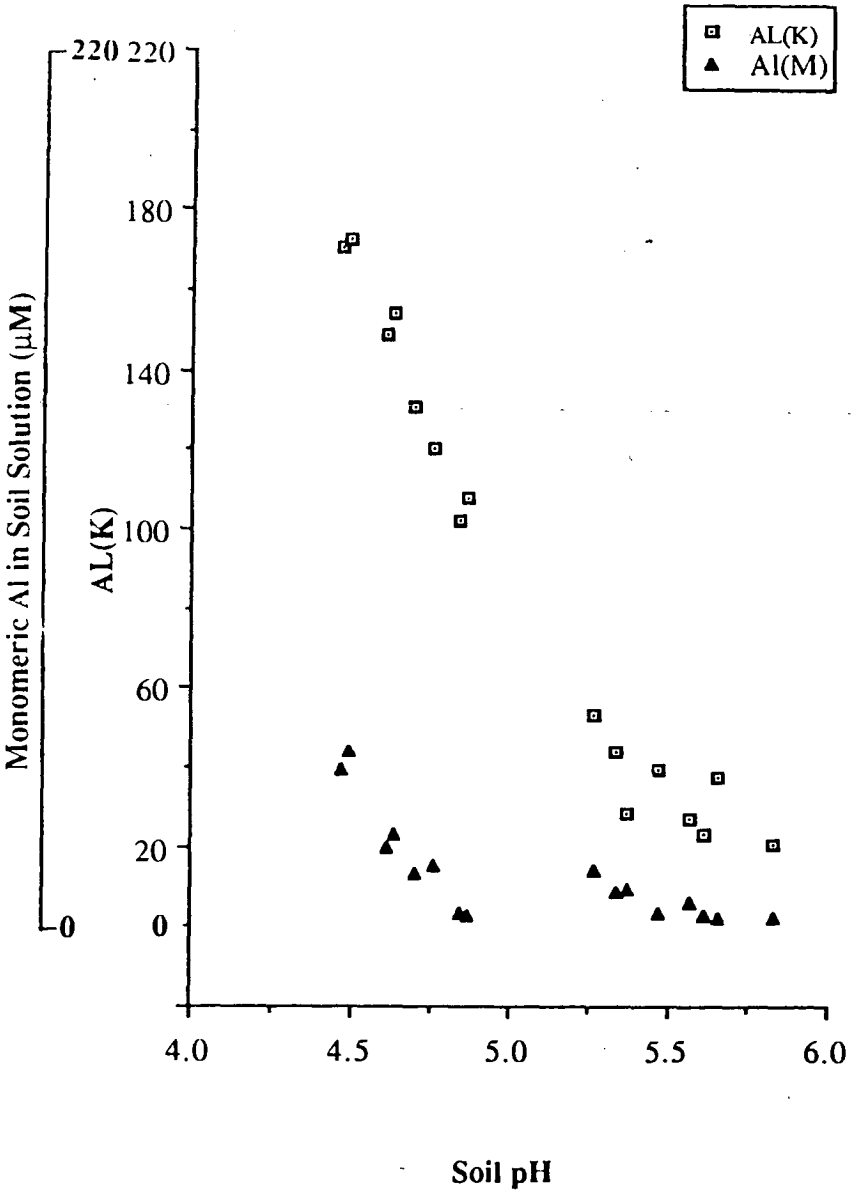


Figure 5.7 Level of exchangeable aluminium [Al(K)] and soil solution monomeric aluminium [Al(M)] in relation to soil pH.

This is in agreement with the results of Magistad (1925), Pierre et al. (1932), and McLean (1976). Soil pH was maintained at higher levels ($P<0.01$) by added organic matter, so the exchangeable and soil solution levels of aluminium were much lower (Table 5.1, 5.2). This effect may be due to release of organic anions and/or sorption of organic complexes on soil particle surfaces (Ritchie and Dolling, 1985). There was no difference ($P>0.05$) in effect on soil pH due to kind of added organic matter.

Phosphorus: Available P (bicarbonate-extractable) and P in the soil solution at approximately pF2 both decreased ($P<0.01$ and $P<0.001$, respectively) with increase in level of Al application (Figure 5.8, 5.9; Table 5.7, 5.8; Appendix 5.4). Both available and solution P levels were lower in the absence of organic matter ($P<0.05$ and $P<0.001$, respectively) at all rates of Al application. Lucerne chaff was more effective ($P<0.05$) in enhancing P levels than barley straw.

It would be expected that aluminium added in solution as the Al^{3+} ion would react with orthophosphate ions (e.g. $H_2PO_4^-$, HPO_4^{2-}) in the soil solution to form insoluble compounds. Bohn and Peech (1969) found that phosphatoaluminium complexes, mostly $AlH_2PO_4^{2+}$, were the dominant form of phosphate in acid solution.

Addition of Al^{3+} to soil decreases pH and increases the solubility of soil aluminium (McLean, 1976) reflected in the rapid reduction of both pH and soil solution P (Figure 5.10). Over the pH range 3 to 7, the monovalent ion $H_2PO_4^-$ is the predominant phosphate anion in the soil solution (Hagen and Hopkins, 1955). Therefore, the greater the amount of added soluble aluminium, the greater will be the amounts of both available and solution P reacting with Al to form insoluble complexes. Addition of organic matter was followed by the appearance of larger amounts of both exchangeable and solution P compared to soils without added organic matter, with lucerne chaff having a much greater effect than barley straw. These differences were maintained as P levels fell at about the same rate in response to addition of soluble Al and may be related to differences in the amount and type of organic anions released during decomposition of the two types of organic matter

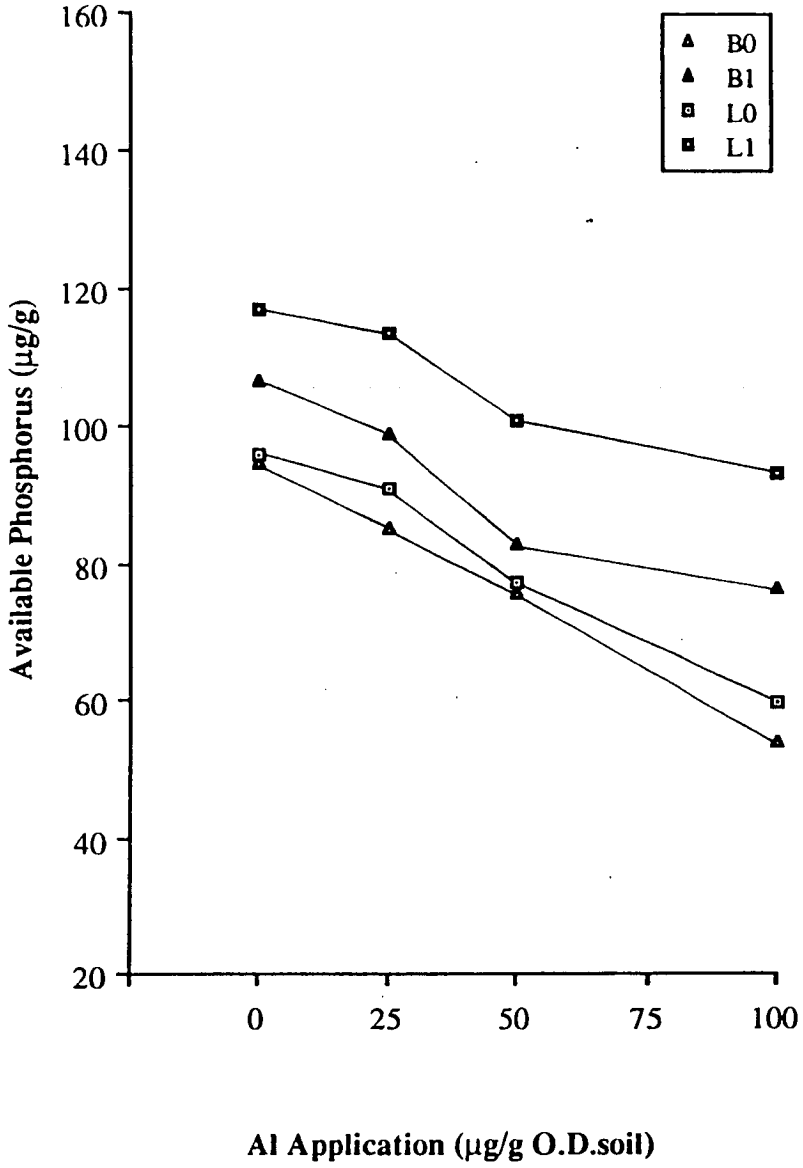


Figure 5.8 Relationship between level of aluminium applied as $Al_2(SO_4)3.14H_2O$ and available P with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

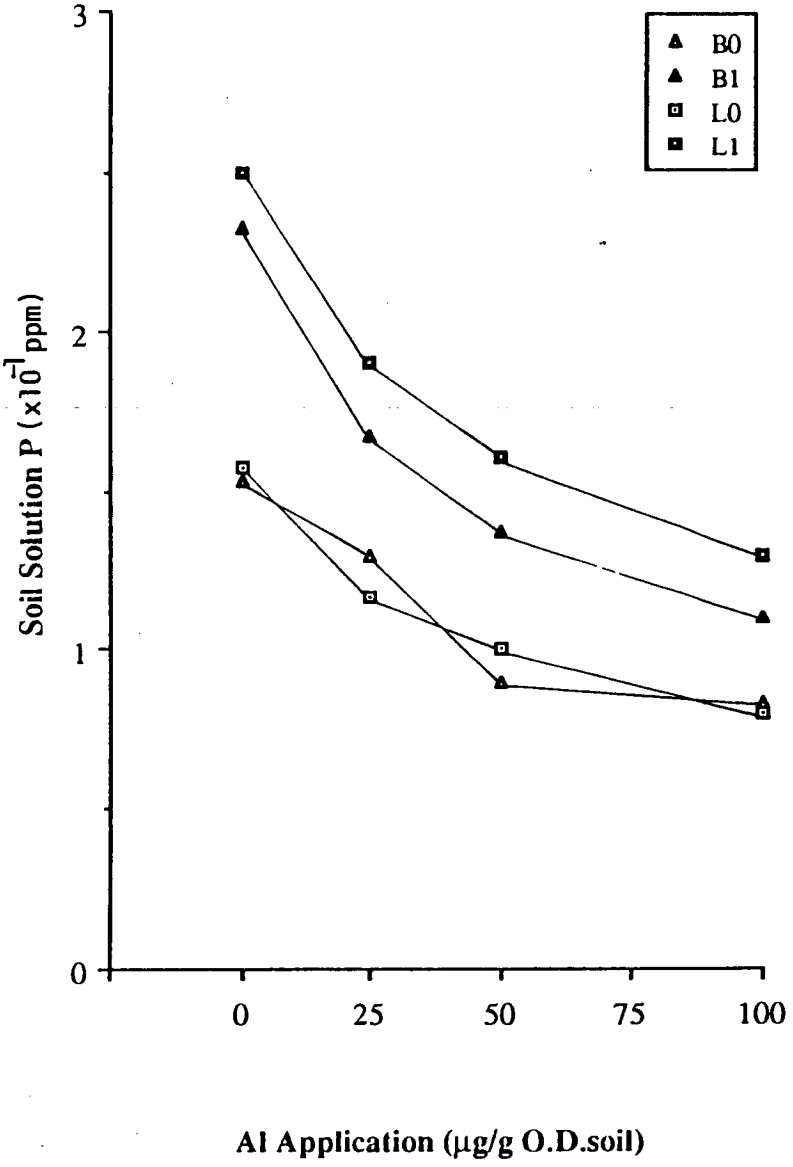


Figure 5.9 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and soil solution P (pF2) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.7 Level of available P in relation to type and rate of organic matter and level of Al application (Means of three replicates).

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	100.79	92.17	79.35	65.38	84.42
Lucerne chaff	106.41	102.25	89.0	76.48	93.53
mean (A)	103.6	97.21	84.17	70.93	

LSD (0.05); O.M. type (T) = 8.52 * T x A = NS
Al application (A) = 15.91 **

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	95.39	88.09	76.4	56.93	79.21
With O.M.	111.79	106.31	91.94	84.93	98.74

LSD (0.05); O.M. rate (R) = 13.26 * R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	77.43	91.41	84.42
Lucerne chaff	80.99	106.08	93.53

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	94.8	85.2	75.6	54.1	106.8	99.1	83.1	76.6
Lucerne chaff	96.0	91.0	77.2	59.7	116.8	113.5	100.8	93.2

LSD (0.05); T x R x A = NS

Table 5.8 Levels of P in soil solution (pF2) in relation to type and rate of organic matter and level of Al application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1.93	1.48	1.13	0.97	1.38
Lucerne chaff	2.03	1.53	1.30	1.05	1.48
mean (A)	1.98	1.50	1.22	1.01	

LSD (0.05); O.M. type (T) = 0.0028 * T x A = NS
Al application (A) = 0.267 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1.55	1.23	0.95	0.81	1.13
With O.M.	2.41	1.78	1.48	1.20	1.72

LSD (0.05); O.M. rate (R) = 0.098 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	1.14	1.62	1.38
Lucerne chaff	1.13	1.83	1.48

LSD (0.05); T x R = 0.14 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1.53	1.30	0.90	0.83	2.33	1.67	1.37	1.10
Lucerne chaff	1.57	1.17	1.00	0.80	2.50	1.90	1.60	1.30

LSD (0.05); T x R x A = NS

Note: The analysis of variance was calculated based on multiplication-transformed data (x 10^{-1})

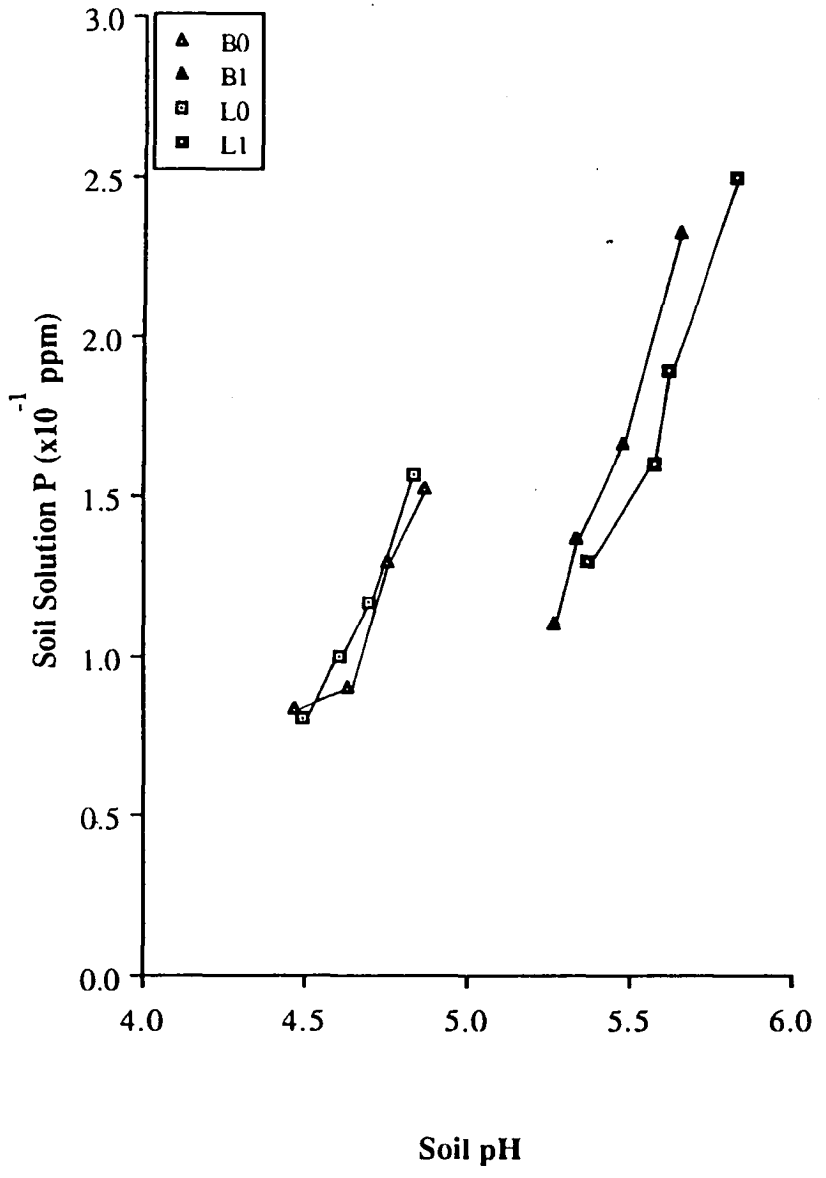


Figure 5.10 Relationship between soil pH and level of P in soil solution with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

used. Futhermore, it is possible that soluble Al was complexed or chelated preferentially by organic acids and thus did not combine with phosphate (Traina et al., 1986).

Phosphorus in plant materials: A small increase ($P>0.05$) in P concentration and content of plant tops was measured at the 25 ppm level of applied aluminium both with and without added organic matter. Thereafter all plant top P concentrations and contents fell sharply ($P<0.001$) (Figure 5.11, 5.12; Table 5.9, 5.10; Appendix 5.5). However, phosphorus concentrations and contents in plant tops were much higher after addition of organic matter ($P<0.01$) and the effect of lucerne chaff was greater than that of barley straw.

Generally, the effect of aluminium on phosphorus has been given more attention than any other nutritional effect involving crop plants. The present results indicated that aluminium depressed phosphorus uptake. In plants which showed symptoms of aluminium toxicity as well as phosphorus deficiency (Al-100 ppm; Ro-nil O.M.), phosphorus concentrations and contents in plant tops were reduced more than 30 per cent below those for untreated soil controls (Al-0 ppm, Ro-nil O.M.) (Figures 5.11, 5.12). However, when organic matter was added plants took up more phosphorus at all levels of added aluminium and there were no symptoms of aluminium toxicity even at the highest level of added aluminium (Al-100 ppm). This may be due to lower concentrations of active aluminium after complexing with organic anions, as discussed above, so that smaller amounts of phosphorus were precipitated in unavailable forms. Organic matter may also facilitate phosphorus desorption and replacement of soil solution phosphorus as it is taken up (Burd and Martin, 1924).

Low solubility is considered to be one of the factors responsible for reduced phosphate availability to most crop plants grown in acidic soils. In the present experiment, levels of phosphate in soil solution increased with increase in soil pH (Figure 5.10). In accord with this, phosphate uptake by plants also increased both with and without added organic matter (Figure 5.12, 5.13). The relationship between

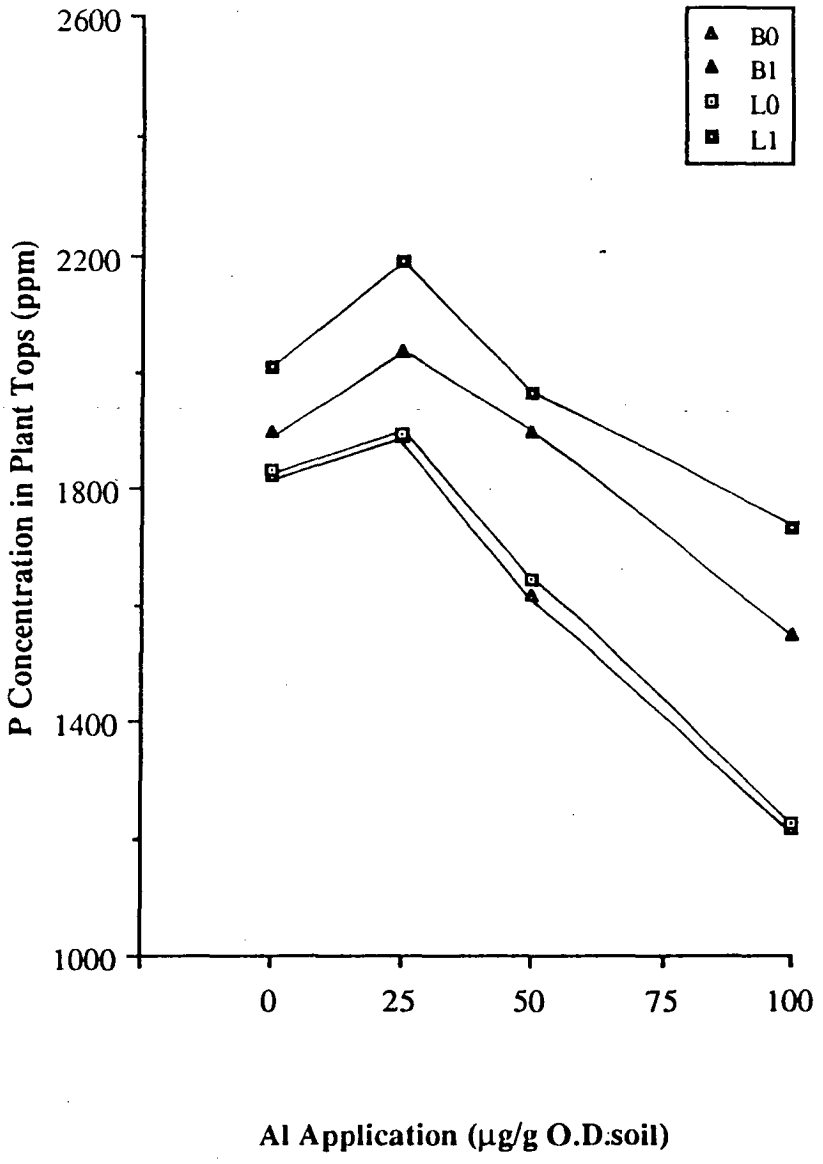


Figure 5.11 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and P content in plant tops with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

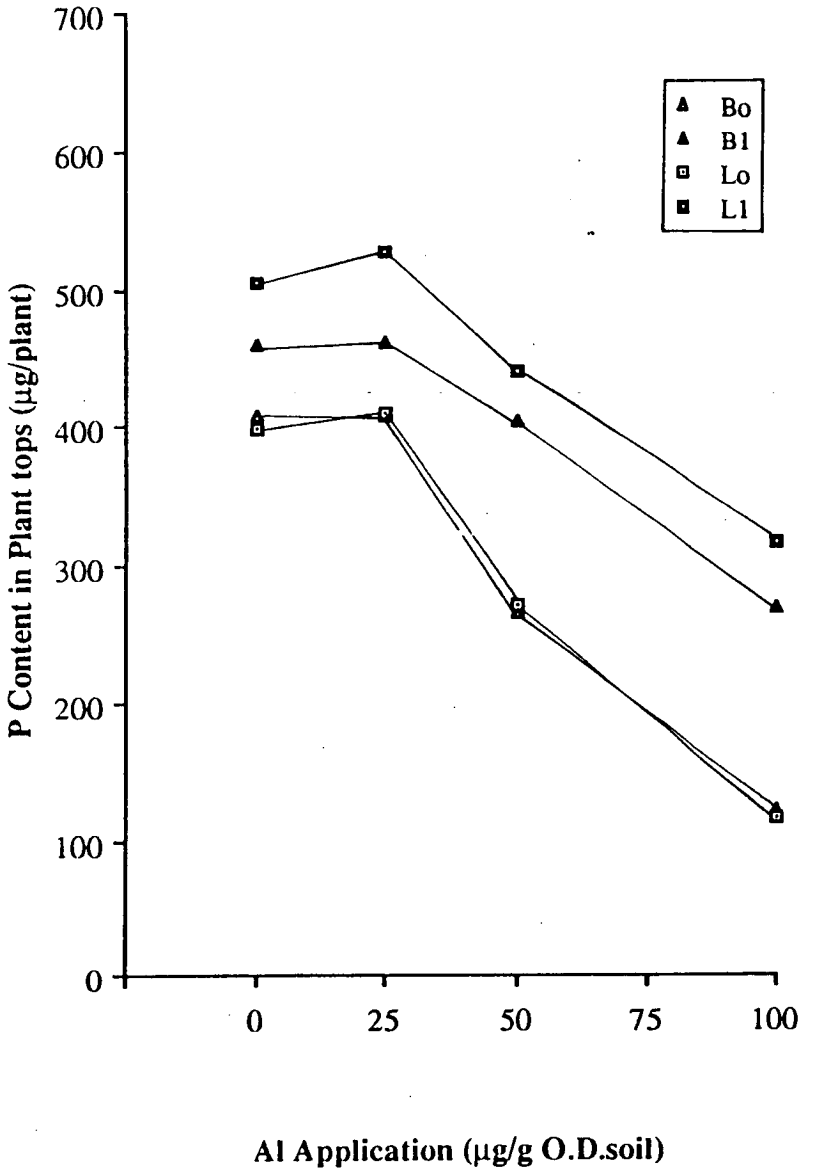


Figure 5.12 Relationship between level of aluminium applied as $Al_2(SO_4)3.14H_2O$ and P content in plant tops with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.9 Phosphorus concentration of plant tops ($\mu gP\ g^{-1}$) in relation to type and rate of organic matter and rate of aluminium application. (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1860.1	1963.5	1758.9	1384.9	1741.9
Lucerne chaff	1919.9	2040.6	1803.2	1479.6	1810.8
mean (A)	1890.0	2002.0	1781.1	1432.3	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 172.16 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1824.8	1891.7	1629.7	1224.1	1642.6
With O.M.	1955.2	2112.4	1932.4	1640.4	1910.1

LSD (0.05); O.M. rate (R) = 95.7 ** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	1636.80	1846.93	1741.86
Lucerne chaff	1648.35	1973.25	1810.80

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1820.2	1889.5	1617.7	1219.8	1900.1	2037.4	1900.2	1550.0
Lucerne chaff	1829.4	1893.9	1641.7	1228.4	2010.3	2187.3	1964.6	1730.8

LSD (0.05); T x R x A = NS

Table 5.10 Phosphorus content in plant tops ($\mu gP\ plant^{-1}$) in relation to type of organic matter, rate of organic matter and level of Al application. (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	433.85	435.52	335.00	194.95	349.83
Lucerne chaff	452.03	469.18	356.03	216.48	373.43
mean (A)	442.94	452.35	345.51	205.71	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 47.11 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	404.13	409.18	268.75	118.61	300.17
With O.M.	481.75	495.52	422.28	292.81	423.09

LSD (0.05); O.M. rate (R) = 17.98 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	301.31	398.35	349.83
Lucerne chaff	299.03	447.83	373.43

LSD (0.05); T x R = 25.43 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	408.87	408.77	265.8	121.80	458.83	462.27	404.20	268.10
Lucerne chaff	399.40	409.60	271.7	115.43	504.67	528.77	440.37	317.53

LSD (0.05); T x R x A = NS

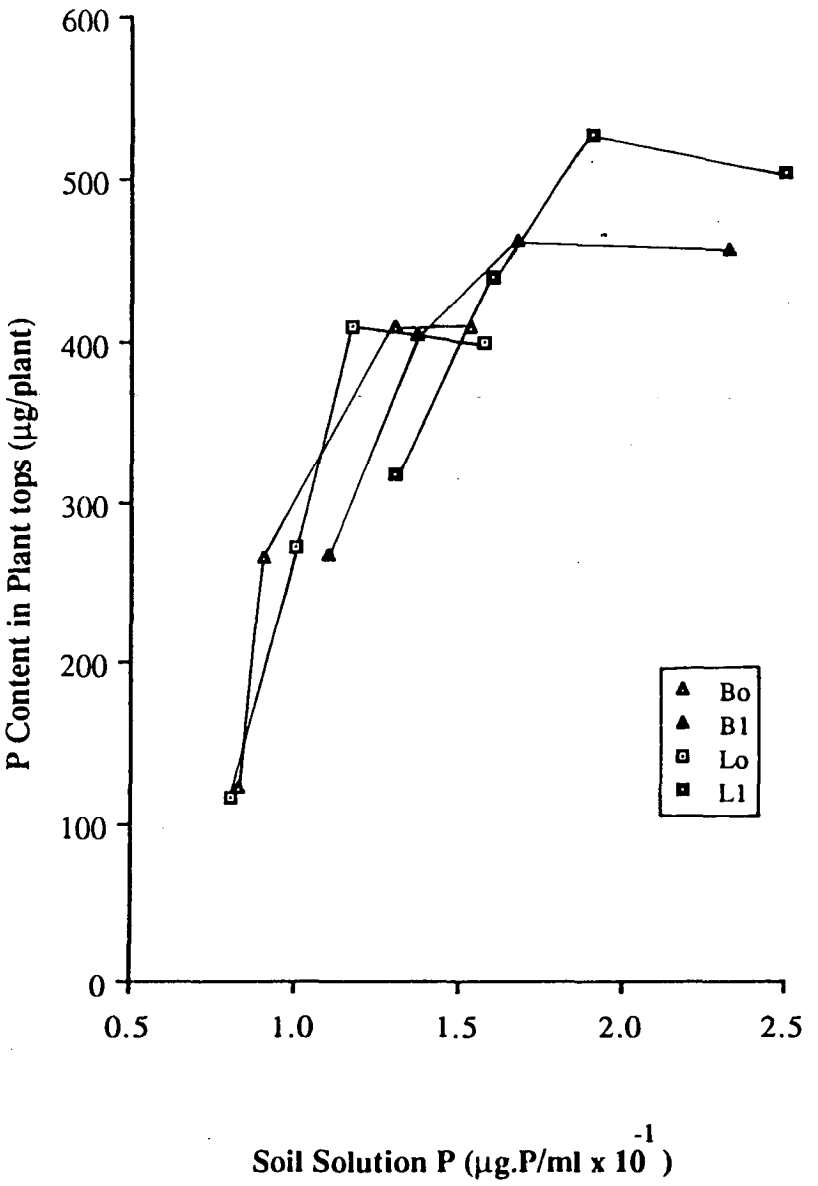


Figure 5.13 Relationship between P content of plant tops and soil solution P with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

dry weight of roots and tops and level of soil solution phosphate followed a similar trend and highest yields were obtained when soil solution phosphate was 0.2 to 0.25 µgP/ml (Figure 5.14 and 5.15, respectively).

Plant dry matter production and symptoms of aluminium toxicity: Symptoms of aluminium toxicity were apparent in tops and roots only at the highest rate of aluminium application without added organic matter (Al-100 ppm; Ro). The symptoms were similar to those described by Foy (1974).

The dry weight of tops progressively decreased ($P<0.001$) with increasing level of aluminium application both with and without added organic matter (Figure 5.16; Table 5.11; Appendix 5.6). However, this decrease was much less ($P<0.001$) in the presence of added organic matter.

The highest yield of plant tops was obtained in response to organic matter added as lucerne chaff (Al-0 ppm, L1). These yields were assigned a value of 100 and yields of other treatments were calculated as percentages (Figure 5.17). The control treatments (A-o ppm, Lo, Bo) yielded approximately 90 per cent of maximum yield. The relative yield of plant tops was reduced progressively with increase in added aluminium. At the highest rate of aluminium application (100 ppm) without organic matter the yield was reduced by more than 50 per cent showing clearly that aluminium was a severely growth-limiting factor. However, the effect of aluminium was much less ($P<0.001$) in the presence of added organic matter with plant tops dry matter production reaching 60-70 per cent of the highest yield even at the highest level of added aluminium. Evidently aluminium stress was largely overcome by addition of organic matter.

Root dry weights showed even greater effects of added aluminium ($P<0.001$) on the one hand and of added organic matter in mitigating the effect of aluminium ($P<0.01$) on the other (Figures 5.18, 5.19; Table 5.12; Appendix 5.6).

5.3.2. Sequence (b)

Aluminium: Exchangeable aluminium increased ($P<0.001$) with rate of application of aluminium as $Al_2(SO_4)_3 \cdot 14H_2O$ (Figure 5.20; Appendix 5.7).

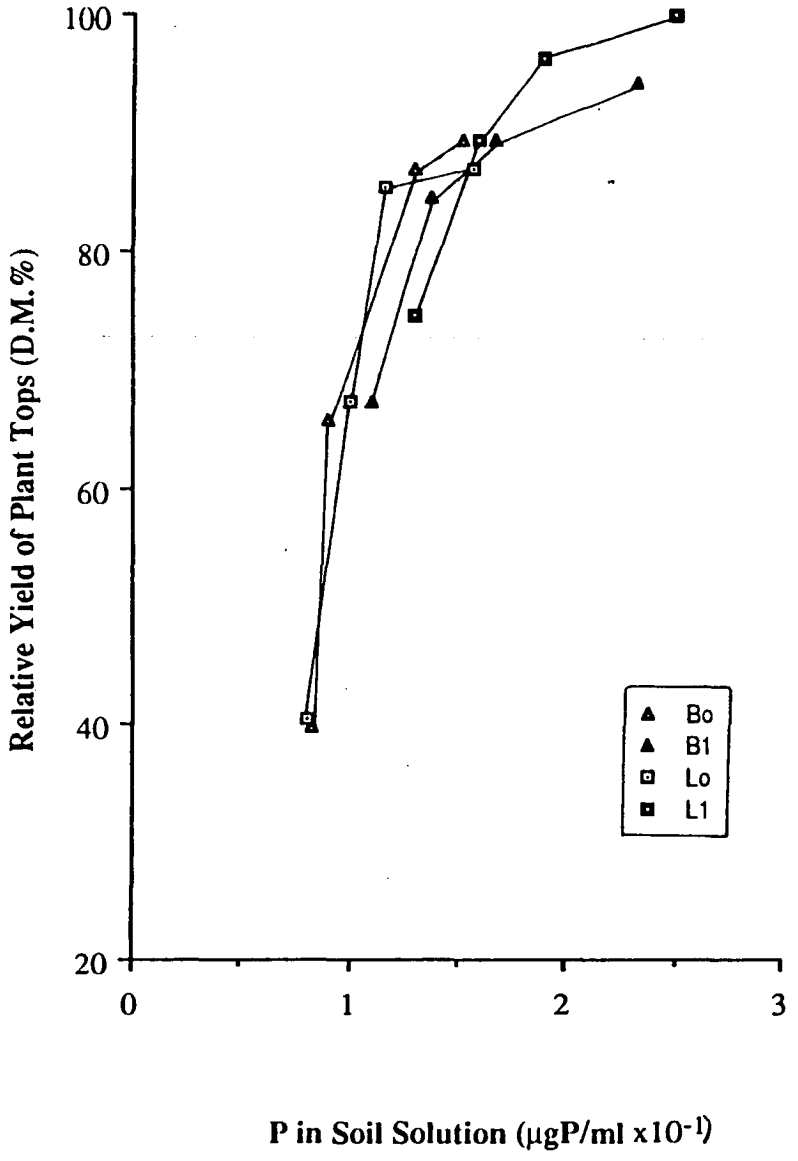


Figure 5.14 Relationship between level of P in soil solution and relative yield of plant top dry weight (D.M.%) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).(Relative yield calculated as described on P. 104 above)

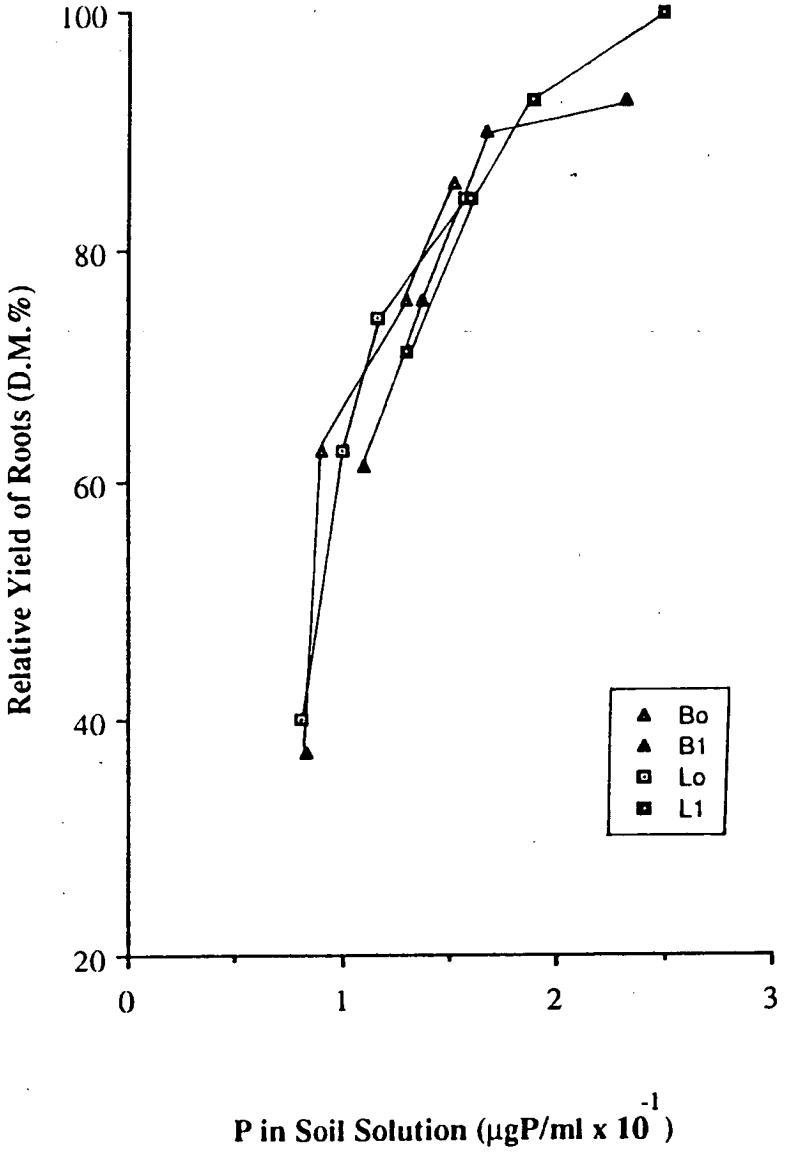


Figure 5.15 Relationship between level of P in soil solution and relative yield of root dry weight (D.M.%) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).(Relative yield calculated as described on P. 104 above)

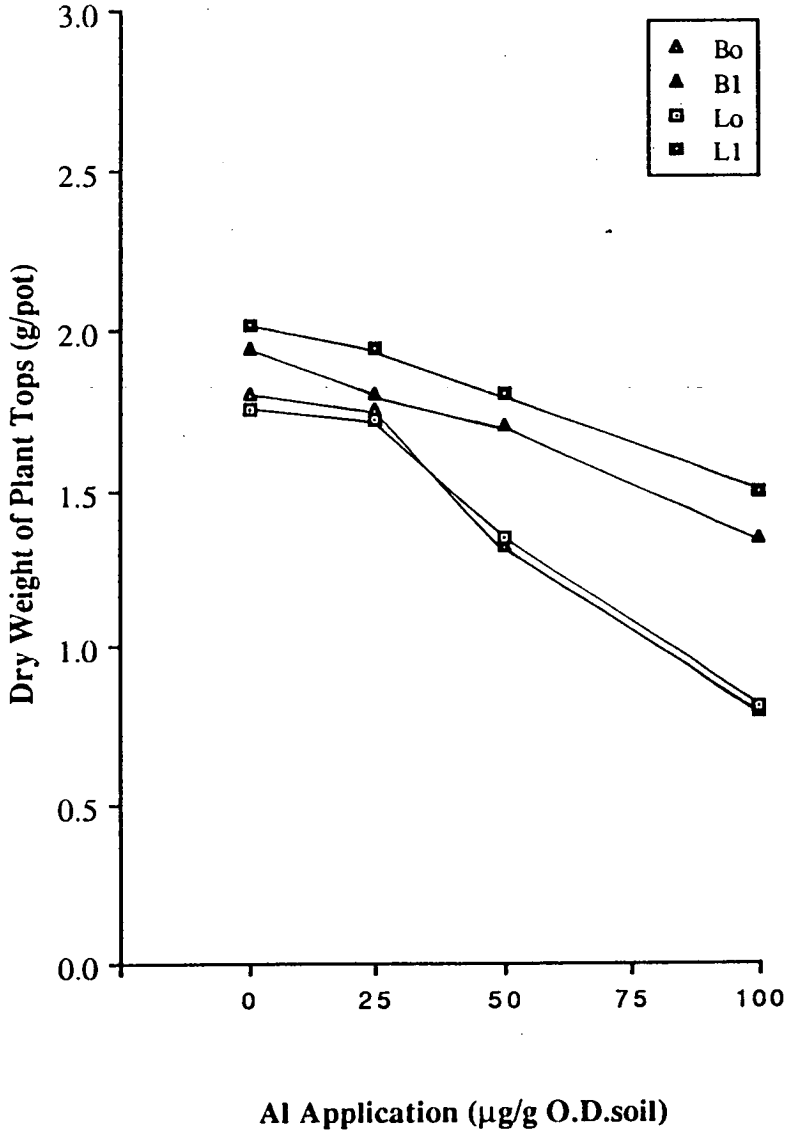


Figure 5.16 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and dry weight of plant tops with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.11 Dry weight of plant tops (g pot^{-1}) in relation to type of organic matter, rate of organic matter and level of Al application (Mean of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1.87	1.78	1.51	1.08	1.56
Lucerne chaff	1.88	1.83	1.58	1.16	1.61
mean (A)	1.87	1.80	1.54	1.12	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.17 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1.77	1.73	1.33	0.80	1.41
With O.M.	1.97	1.87	1.74	1.42	1.75

LSD (0.05); O.M. rate (R) = 0.05 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	1.42	1.70	1.56
Lucerne chaff	1.41	1.81	1.61

LSD (0.05); T x R = 0.07 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1.80	1.75	1.32	0.80	1.94	1.80	1.69	1.35
Lucerne chaff	1.75	1.72	1.35	0.81	2.00	1.94	1.80	1.50

LSD (0.05); T x R x A = NS

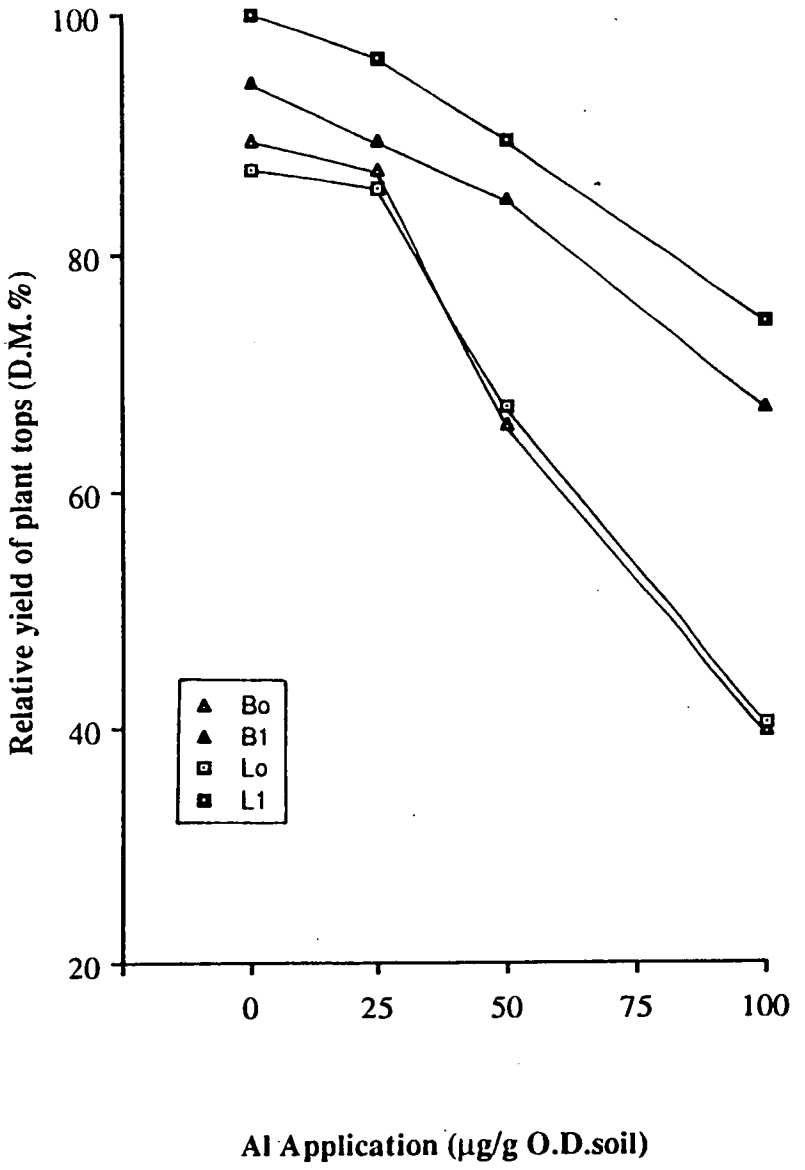


Figure 5.17 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and relative yield of plant tops (D.M.%) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).(Relative yield calculated as described on P.104 above).

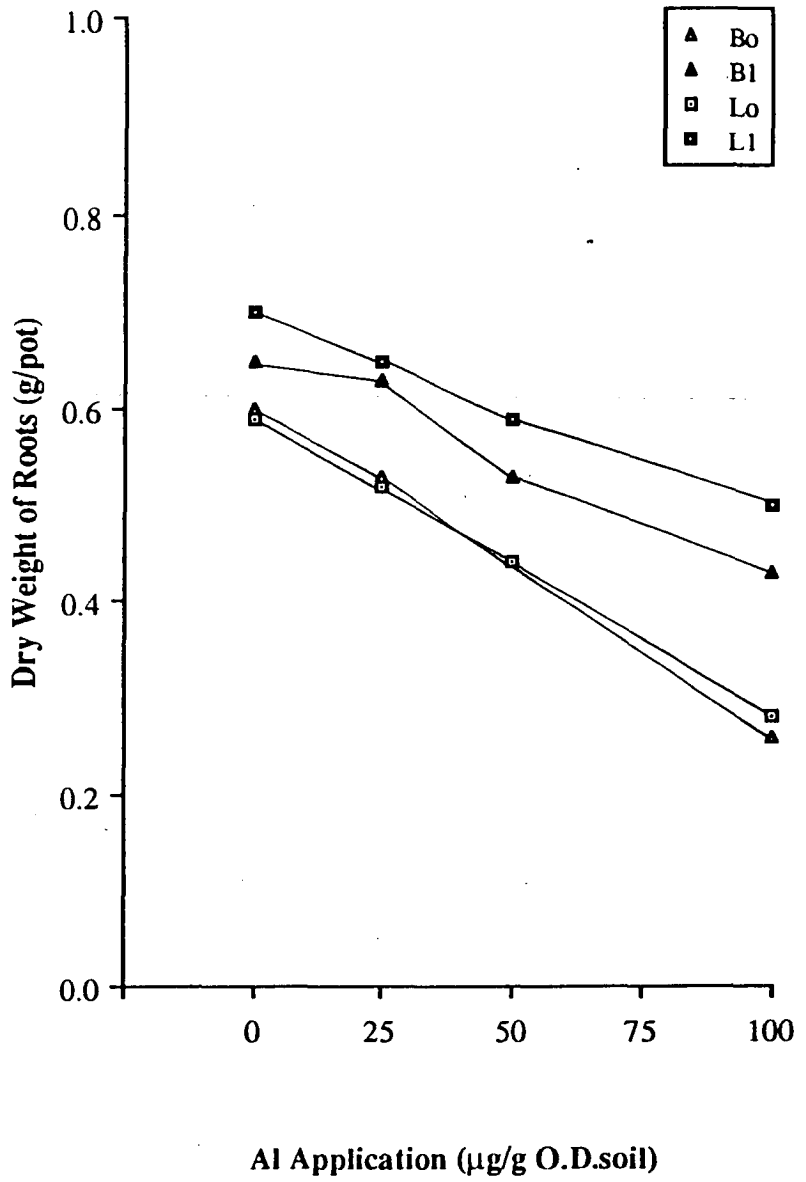


Figure 5.18 Relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and dry weight of roots with and without added organic matter as barley straw (B1, Bo) or lucerne chaff(L1, Lo).

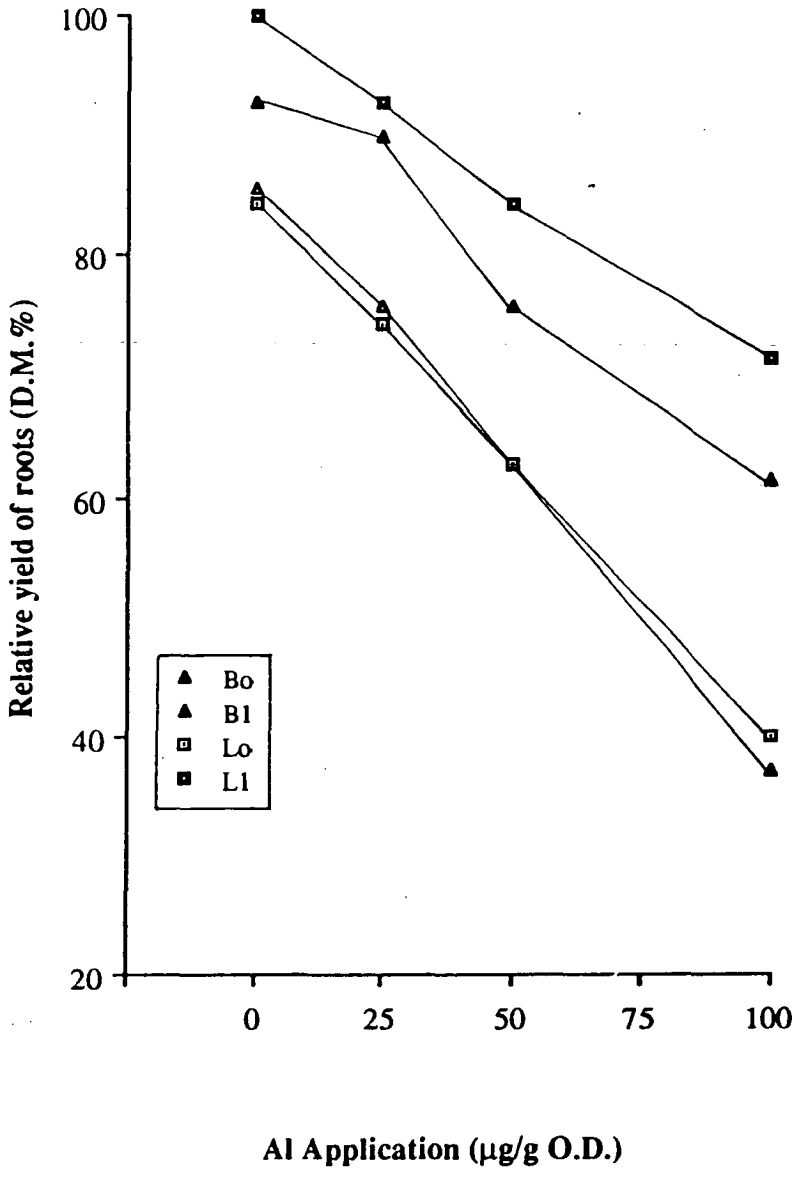


Figure 5.19 The relationship between level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ and relative yield of roots (D.M.%) with and without added organic matter as barley straw (B1, Bo) or.luceme chaff (L1, Lo).(Relative yield calculated as described on P.104above).

Table 5.12 Root dry weight (g pot^{-1}) in relation to type of organic matter, rate of organic matter and level of Al application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	0.63	0.58	0.49	0.35	0.51
Lucerne chaff	0.65	0.59	0.52	0.39	0.53
mean (A)	0.64	0.58	0.50	0.37	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.08 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	0.59	0.52	0.44	0.27	0.46
With O.M.	0.68	0.64	0.56	0.46	0.58

LSD (0.05); O.M. rate (R) = 0.07 ** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	0.46	0.56	0.51
Lucerne chaff	0.46	0.61	0.53

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	0.60	0.53	0.44	0.26	0.65	0.63	0.53	0.43
Lucerne chaff	0.59	0.52	0.44	0.28	0.70	0.65	0.59	0.50

LSD (0.05); T x R x A = NS

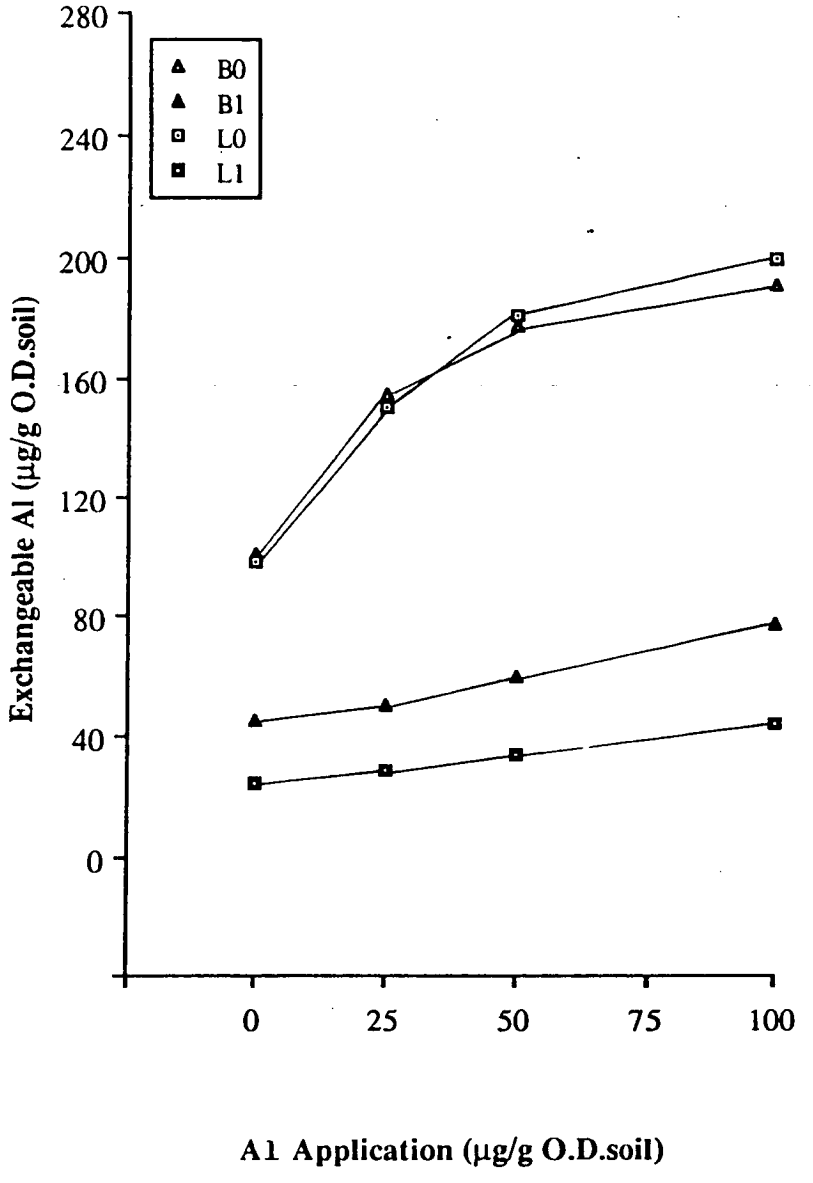


Figure 5.20 Relationship between exchangeable aluminium (1 M KCl) and level of aluminium applied as $Al_2(SO_4)3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Exchangeable aluminium was much lower ($P<0.001$) at all levels of aluminium application in the presence of added organic matter. Lucerne chaff was more effective ($P<0.05$) than barley straw in reducing levels of exchangeable aluminium (Table 5.13). Without added organic matter exchangeable aluminium increased rapidly at first and then more slowly. This may be explained in terms of immediate replacement of other exchangeable cations followed by reduction of pH, buffering, and slower entry of aluminium within the exchange complex or the formation of non-exchangeable complexes. Of course much of the applied aluminium at the higher levels may be accounted for as monomeric aluminium remaining in soil solution (Figure 5.21). Increases in both exchangeable and monomeric aluminium after addition of organic matter were relatively small, and linear over the range of aluminium application.

Similar effects were measured in respect of monomeric aluminium in the soil solution (Figure 5.21; Table 5.14; Appendix 5.7). Without added organic matter the level of monomeric aluminium in the soil solution increased sharply ($P<0.001$) with rate of aluminium application of $Al_2(SO_4)_3 \cdot 14H_2O$. With added organic matter both the magnitude and rate of increase were much less ($P<0.001$). Lucerne chaff appeared to be slightly more effective than barley straw over the whole range of aluminium application but the difference was not significant ($P>0.05$).

Organically complexed aluminium in the soil solution also increased much more ($P<0.01$) with rate of application of aluminium in the presence of added organic matter than in its absence, with barley straw performing almost equally with lucerne chaff, especially at the higher rates of aluminium application (Figure 5.22a; Table 5.15; Appendix 5.8). While total aluminium in the soil solution increased ($P<0.001$) with level of aluminium application, differences due to organic matter addition were not significant ($P>0.05$).(Figure 5.22b; Table 5.16; Appendix 5.8).

The results show that the added soluble aluminium was distributed in both exchanger and solution phases and that much of the latter was in the form of soluble organic complexes in the presence of added organic matter. Thus the results from

Table 5.13 Exchangeable Al in relation to type of organic matter, rate of organic matter and level of Al application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	72.97	102.49	119.03	134.72	107.3
Lucerne chaff	61.85	89.29	107.38	121.90	95.10
mean (A)	67.41	95.89	113.2	128.31	

LSD (0.05); O.M. type (T) = 7.46 * T x A = NS
Al application (A) = 9.91 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	99.86	152.31	179.11	195.5	156.69
With O.M.	34.96	39.47	47.29	61.11	45.71

LSD (0.05); O.M. rate (R) = 9.36 *** R x A = 35.91 *

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	156.12	58.48	107.3
Lucerne chaff	157.27	32.94	95.10

LSD (0.05); T x R = 13.24 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	100.9	154.7	177.5	191.5	45.1	50.3	60.6	78.0
Lucerne chaff	98.9	149.9	180.8	199.5	24.9	28.6	34.0	44.3

LSD (0.05); T x R x A = NS

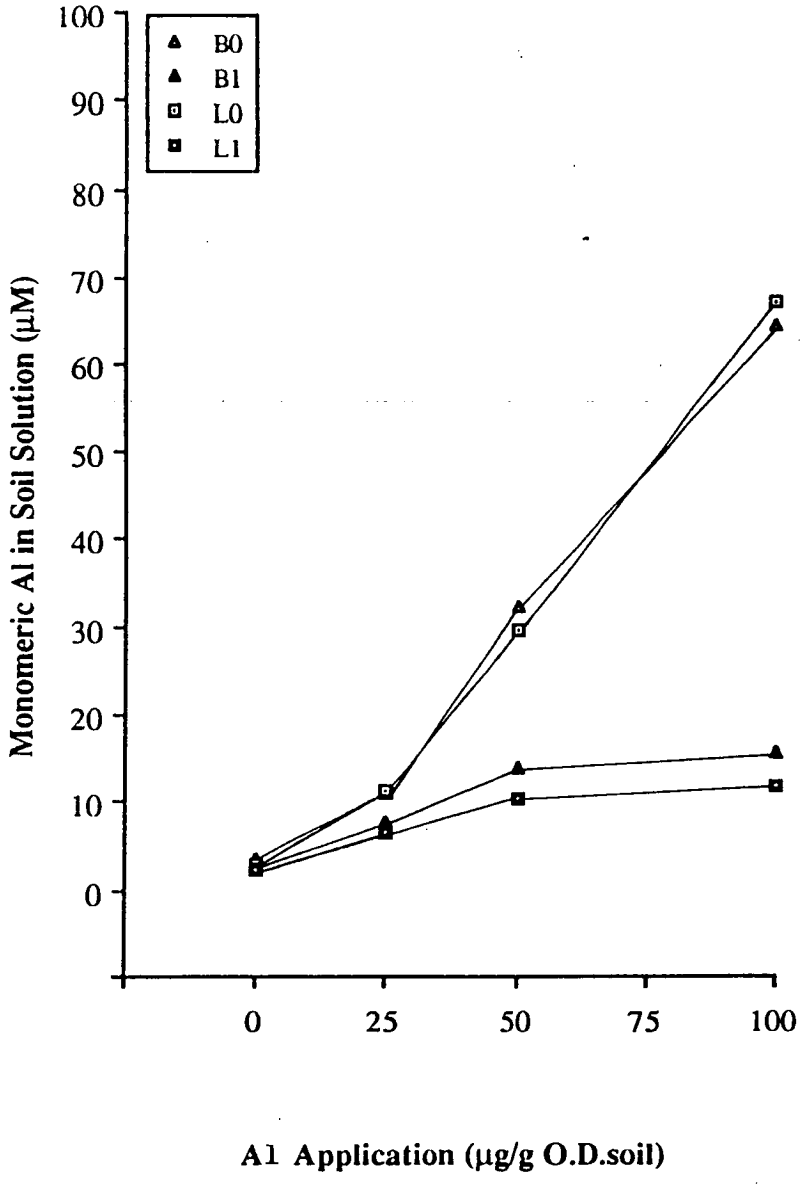


Figure 5.21 Relationship between monomeric aluminium in the soil solution (pF2) and level of aluminium applied as $Al_2(SO_4)3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.14 Monomeric Al (μM) in soil solution in relation to type and rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	2.95	9.3	23.03	40.13	18.85
Lucerne chaff	2.59	8.89	20.02	39.63	17.78
mean (A)	2.77	9.09	21.52	39.88	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 3.38 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	3.18	11.17	30.87	65.93	27.79
With O.M.	2.36	7.01	12.18	13.83	8.85

LSD (0.05); O.M. rate (R) = 1.74*** R x A = 5.9 ***

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	27.80	9.91	18.85
Lucerne chaff	27.78	7.79	17.78

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	3.46	10.93	32.20	64.61	2.44	7.67	13.86	15.66
Lucerne chaff	2.90	11.42	29.54	67.26	2.29	6.35	10.50	12.00

LSD (0.05); T x R x A = NS

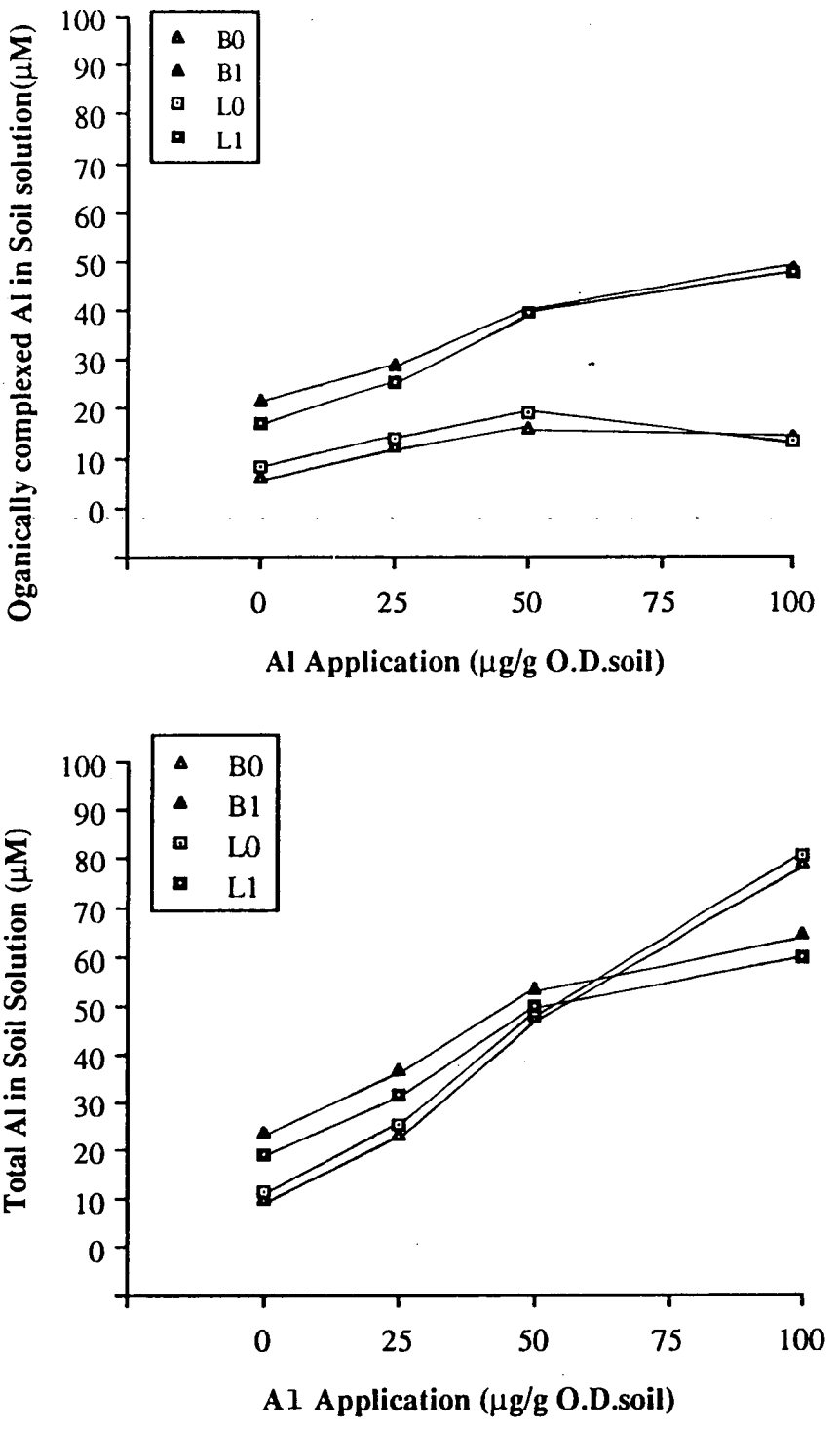


Figure 5.22 Relationship between (a) organically complexed aluminium and (b) total aluminium, in the soil solution (pF2), and level of aluminium applied as $Al_2(SO_4)3.14H_2O$ with and without added organic matter applied as barley straw (Bo, B1) or lucerne chaff (Lo, L1).

Table 5.15 Organically complexed Al (μM) in soil solution (pF2) in relation to type and rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	13.98	20.90	27.73	31.69	23.57
Lucerne chaff	12.66	19.84	29.36	30.62	73.12
mean (A)	13.32	20.37	28.54	31.15	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 3.59 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	7.40	13.33	17.51	14.06	13.08
With O.M.	19.22	27.40	39.57	48.24	33.61

LSD (0.05); O.M. rate (R) = 1.33 *** R x A = 8.21 **

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	12.37	34.78	23.57
Lucerne chaff	13.79	32.45	23.12

LSD (0.05); T x R = 1.88 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	6.37	12.55	15.89	14.65	21.58	29.24	39.56	48.73
Lucerne chaff	8.44	14.11	19.14	13.47	16.87	25.57	39.58	47.76

LSD (0.05); T x R x A = NS

Table 5.16 Total Al (μM) in soil solution (pF2) in relation to type and rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	16.93	30.20	50.76	71.83	42.43
Lucerne chaff	15.25	28.73	49.38	70.25	40.90
mean					
(A)	16.09	29.46	50.07	71.04	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 2.63 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	10.58	24.50	48.38	79.99	40.87
With O.M.	21.59	34.41	51.75	62.07	42.46

LSD (0.05); O.M. rate (R) = NS R x A = 9.92 **

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	40.17	44.69	42.43
Lucerne chaff	41.57	40.23	40.90

LSD (0.05); T x R = 3.88 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	9.83	23.48	48.09	79.26	24.02	36.91	53.42	64.39
Lucerne chaff	11.34	25.53	48.68	80.73	19.16	31.92	50.08	59.76

LSD (0.05); T x R x A = NS

Sequence (b) of the experiment are consistent with those from Sequence (a) and show very clearly the potential of added organic matter as an amendment to detoxify soil aluminium in Burnie clay loam (Evans and Kamprath, 1970; Hoyt and Turner, 1975).

Ionic strength of soil solution: Ionic strength of soil solutions (Gillman and Bell, 1978) increased ($P<0.001$) with rate of application of aluminium as $Al_2(SO_4)_3 \cdot 14H_2O$ (Figure 5.23; Appendix 5.9). Ionic strengths were much greater ($P<0.001$) with added organic matter but the rate of increase with level of applied aluminium was about the same with or without added organic matter (Table 5.17).

Soil reaction (pH 0.002 M $BaCl_2$): .This decreased ($P<0.01$) at about the same rate with increase in level of application of aluminium as $Al_2(SO_4)_3 \cdot 14H_2O$ both with and without added organic matter (Figure 5.24; Appendix 5.9). Soil reaction was about one unit of pH higher with than without added organic matter ($P<0.05$) (Table 5.18) and this relationship is consistent with that found for Sequence (a) of the experiment. It was noted that both exchangeable aluminium and monomeric aluminium in the soil solution (pF2) increased rapidly to high levels at pH's below 4.8 (Figure 5.25).

Phosphorus: Increasing the level of aluminium application decreased ($P<0.001$) both available (0.5 M $NaHCO_3$, pH 8.5) and soil solution phosphorus (pF2) (Figure 5.26, 5.27; Appendix 5.10).

Levels of P in both phases were greater following addition of organic matter ($P<0.001$) at all levels of added aluminium. Also, lucerne chaff was more effective ($P<0.01$) in enhancing available and soil solution P than barley straw (Table 5.19, 5.20).

The results were in accord with those for Sequence (a) of the overall experiment. Reduced levels of P were again considered to be due to increased soil acidity and activity of aluminium.

Phosphorus in plant materials: The concentrations of phosphorus in plant tops in both the presence and absence of added organic matter increased

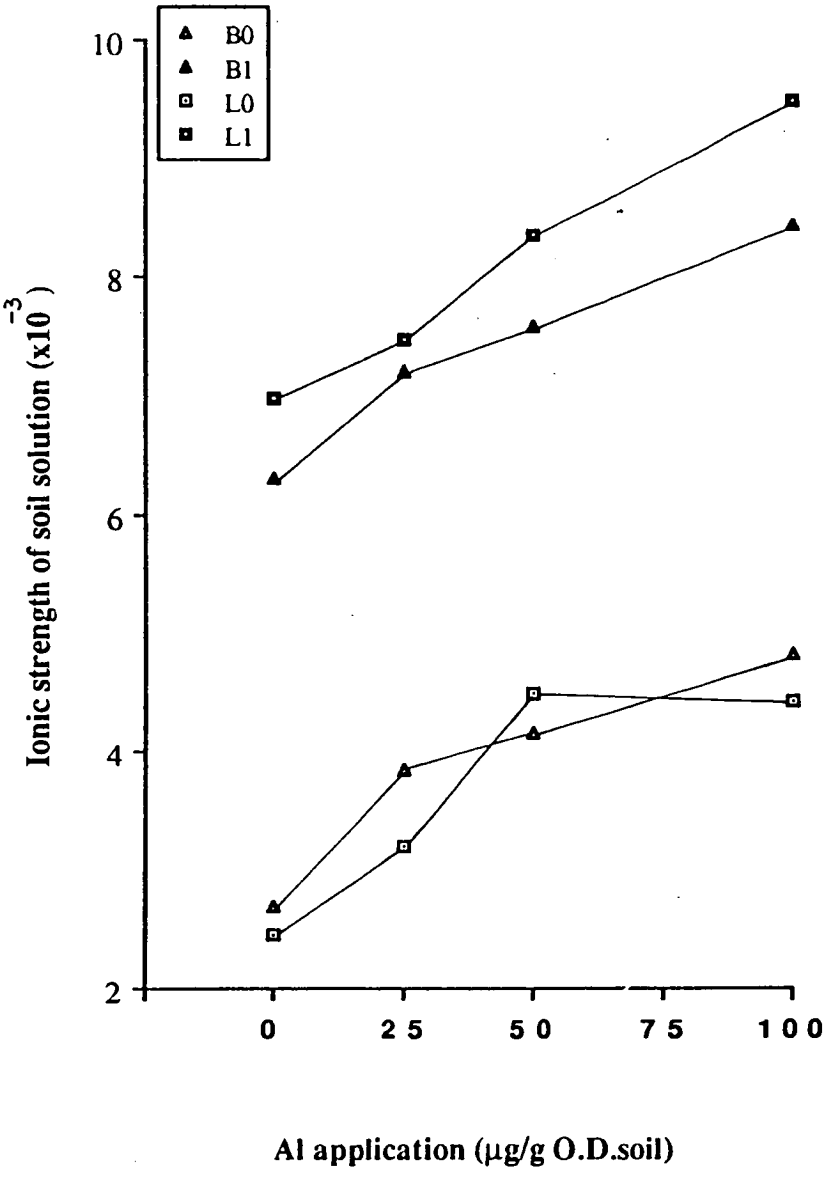


Figure 5.23 Relationship between ionic strength of soil solution (pF2) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.17 Ionic strength of soil solution (Gillman and Bell, 1978) in relation to type of organic matter, rate of organic matter and level of Al application (Means of three replicates $x10^{-3}$)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	4.51	5.52	5.87	6.63	5.63
Lucerne chaff	4.72	5.35	6.41	6.96	5.86
mean (A)	4.61	5.43	6.14	6.79	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.56 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	2.58	3.53	4.32	4.62	3.76
With O.M.	6.65	7.33	7.96	8.97	7.73

LSD (0.05); O.M. rate (R) = 1.25 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	3.89	7.38	5.63
Lucerne chaff	3.64	8.07	5.86

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	2.70	3.85	4.17	4.83	6.33	7.20	7.58	8.44
Lucerne chaff	2.46	3.22	4.48	4.42	6.97	7.47	8.34	9.50

LSD (0.05); T x R x A = NS

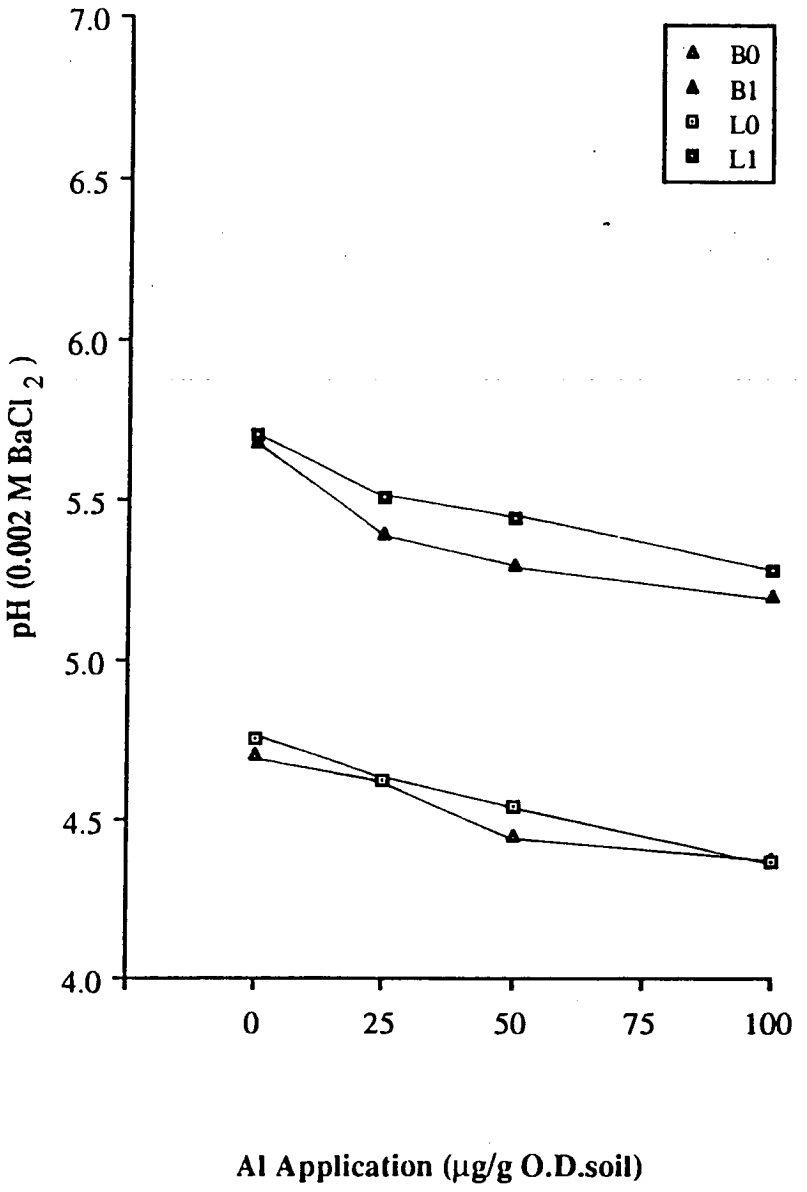


Figure 5.24 Relationship between soil reaction (pH 0.002 M $BaCl_2$) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.18 Soil reaction (pH 0.002 M $BaCl_2$) in relation to type and rate of organic matter and level of aluminium application (Means of three replicates).

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	5.19	5.0	4.88	4.79	4.97
Lucerne chaff	5.23	5.06	5.0	4.83	5.03
mean (A)	5.21	5.03	4.94	4.81	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.2 **

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	4.73	4.62	4.49	4.37	4.55
With O.M.	5.69	5.45	5.37	5.24	5.44

LSD (0.05); O.M. rate (R) = 0.57 * R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	4.54	5.4	4.97
Lucerne chaff	4.57	5.49	5.03

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	4.70	4.62	4.45	4.38	5.68	5.4	5.30	5.20
Lucerne chaff	4.75	4.62	4.54	4.37	5.71	5.51	5.45	5.28

LSD (0.05); T x R x A = NS

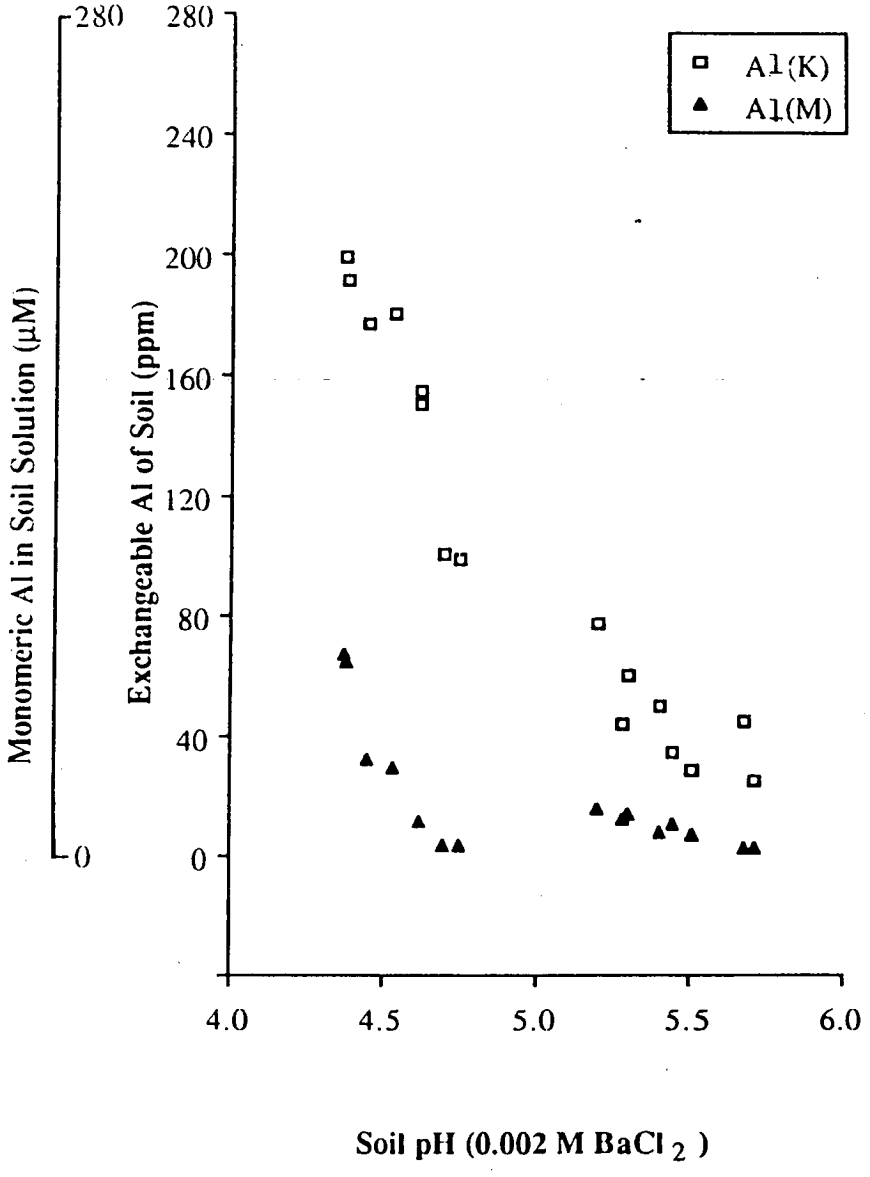


Figure 5.25 Level of exchangeable aluminium [Al(K)] and soil solution monomeric aluminium [Al(M)] in relation to soil pH.

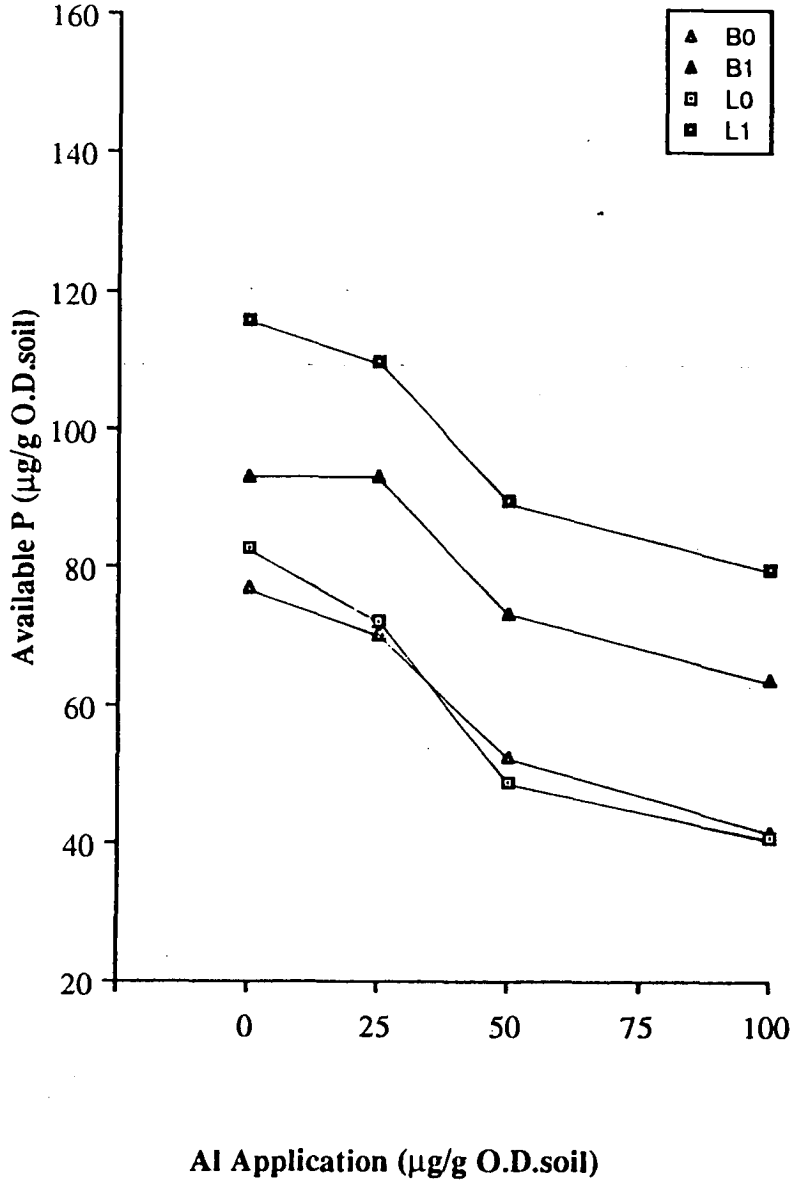


Figure 5.26 Relationship between available phosphorus (0.5M $NaHCO_3$, pH 8.5) and level of aluminium applied as $Al_2(SO_4)3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

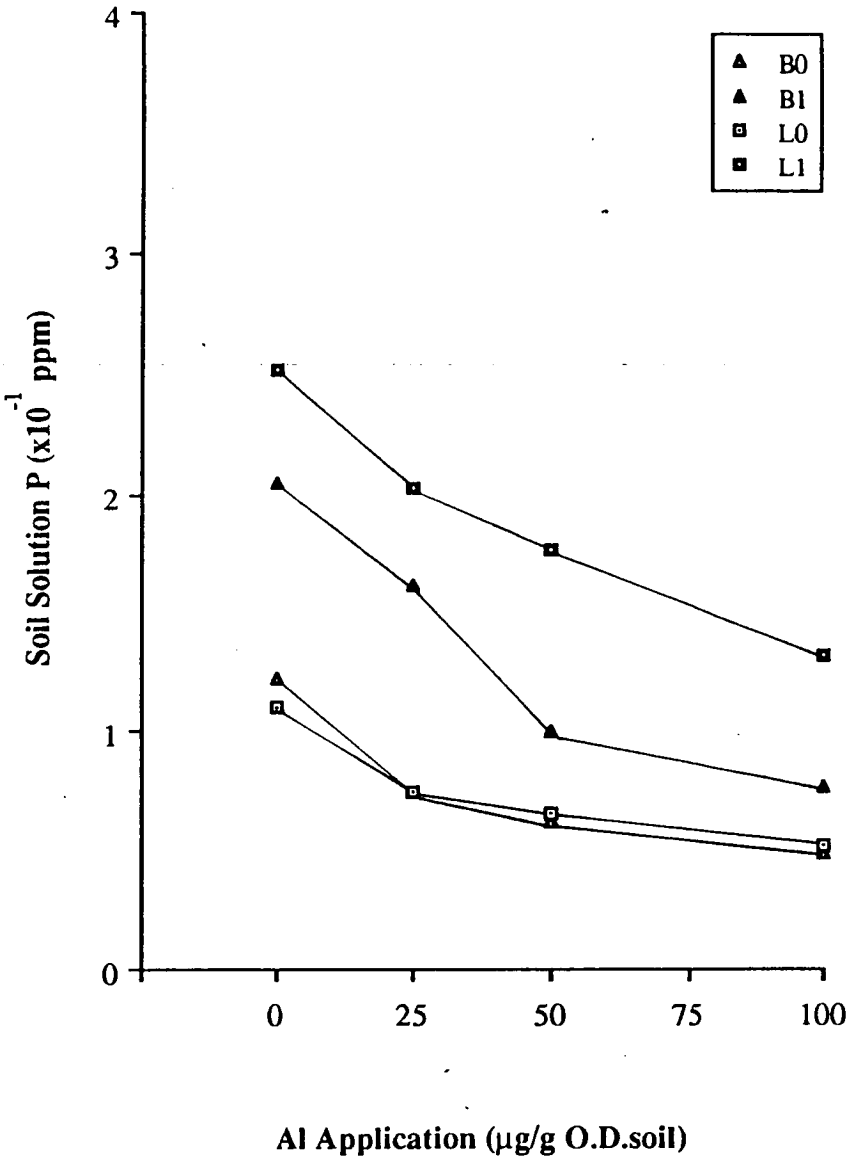


Figure 5.27 Relationship between phosphorus in soil solution (µg/ml x 10^{-1} pF2) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.19 Available phosphorus (µg/g O.D.soil) in relation to type and rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	85.00	81.69	62.94	52.80	70.61
Lucerne chaff	99.29	90.95	69.20	60.28	79.93
mean					
(A)	92.14	86.32	66.07	56.54	

LSD (0.05); O.M. type (T) = 5.51 ** T x A = NS
Al application (A) = 9.71 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	79.99	71.24	50.59	41.19	60.75
With O.M.	104.3	101.4	81.54	71.89	89.78

LSD (0.05); O.M. rate (R) = 7.22 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	60.41	80.81	70.61
Lucerne chaff	61.10	98.76	79.93

LSD (0.05); T x R = 10.22 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	77.00	70.36	52.53	41.75	93.02	93.02	73.35	63.85
Lucerne chaff	82.98	72.12	48.66	40.64	115.6	109.8	89.74	79.93

LSD (0.05); T x R x A = NS

Table 5.20 Phosphorus in soil solution (µg/ml, pF2) in relation to type of organic matter, rate of organic matter and level of Al application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1.64	1.17	0.82	0.63	1.06
Lucerne chaff	1.81	1.39	1.21	0.92	1.33
mean (A)	1.72	1.28	1.01	0.77	

LSD (0.05); O.M. type (T) = 0.12 ** T x A = NS
Al application (A) = 0.19 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1.16	0.74	0.64	0.51	0.76
With O.M.	2.28	1.82	1.38	1.04	1.63

LSD (0.05); O.M. rate (R) = 0.17 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	0.77	1.36	1.06
Lucerne chaff	0.76	1.91	1.33

LSD (0.05); T x R = 0.25 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1.22	0.74	0.62	0.49	2.05	1.61	1.00	0.77
Lucerne chaff	1.10	0.74	0.66	0.53	2.52	2.03	1.76	1.31

LSD (0.05); T x R x A = NS

Note: The analysis of variance was calculated based on multiplication transformed data ($x\ 10^{-1}$)

slightly with level of aluminium application from Al-0 ppm to Al-25 ppm (Figure 5.28; Table 5.21). However, the data for phosphorus content (Figure 5.29; Table 5.22) and dry matter production (Figure 5.34; Table 5.23) show that this increase in phosphorus concentration in plant tops was due to reduced plant growth under early aluminium stress rather than to enhanced phosphorus uptake. Further increase in the level of applied aluminium up to Al-100 ppm sharply decreased ($P<0.001$) both phosphorus concentration and total phosphorus in plant tops in both the presence and absence of added organic matter (Figures 5.28, 5.29; Appendix 5.11). Although the rates of decrease were very similar, both phosphorus concentration and total phosphorus in plant tops were greater ($P<0.001$) in the presence of added organic matter (Tables 5.21, 5.22; Appendix 5.11).

Symptoms of aluminium toxicity of ryegrass observed in this experiment were similar to those attributed to phosphorus deficiency in plant tops reported for other crops (Foy, 1974). In the present study, these symptoms were observed only at the highest level of aluminium application without added organic matter (Al-100 ppm; O.M.-Ro). In plants which showed symptoms of aluminium toxicity and phosphorus deficiency the concentrations and uptake of phosphorus into plant tops were reduced more than 30 percent below the control treatment (Al-0 ppm; O.M.-Ro) (Figures 5.28, 5.29). However, there were no signs of either aluminium toxicity or phosphorus deficiency in the presence of added organic matter even at the highest level of aluminium application (Al-100 ppm; O.M.-R1).

The results suggest a close relationship between phosphorus uptake into plant tops, phosphorus concentrations in the soil solution and soil pH. The concentrations of phosphorus in soil solutions (pF2) increased with pH (Figure 5.30) and were associated with increased total phosphorus of plant tops in both the presence and absence of added organic matter (Figure 5.31). However these effects were greater in the presence of added organic matter. The highest yields of tops and roots of ryegrass were obtained when the concentration of phosphorus in the soil solution

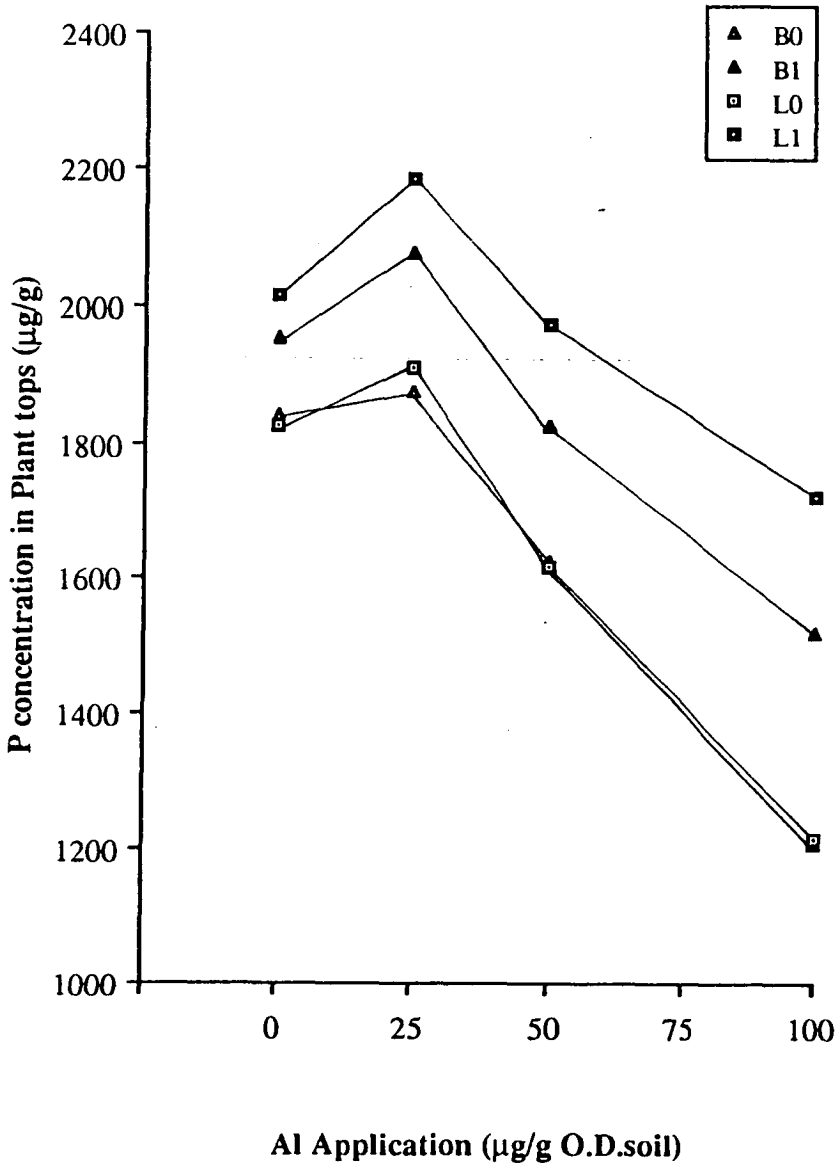


Figure 5.28 Relationship between phosphorus concentration in plant tops (µg/g) and level of aluminium applied as $Al_2(SO_4)3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.21 Phosphorus concentration in plant tops ($\mu gP\ g^{-1}$) in relation to type and rate of organic matter and level of aluminium application. (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1897.7	1976.3	1726.1	1365.7	1741.5
Lucerne chaff	1920.2	2046.2	1794.2	1469.2	1807.4
mean (A)	1908.9	2011.2	1760.1	1417.4	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 210.56 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1833.5	1893.2	1621.7	1213.4	1640.5
With O.M.	1984.4	2129.2	1898.5	1621.5	1908.4

LSD (0.05); O.M. rate (R) = 74.2 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	1638.47	1844.43	1741.45
Lucerne chaff	1642.48	1972.38	1807.43

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1841.2	1877.3	1626.4	1209.0	1954.2	2075.3	1825.8	1522.4
Lucerne chaff	1825.8	1909.2	1617.1	1217.8	2014.6	2183.1	1971.2	1720.6

LSD (0.05); T x R x A = NS

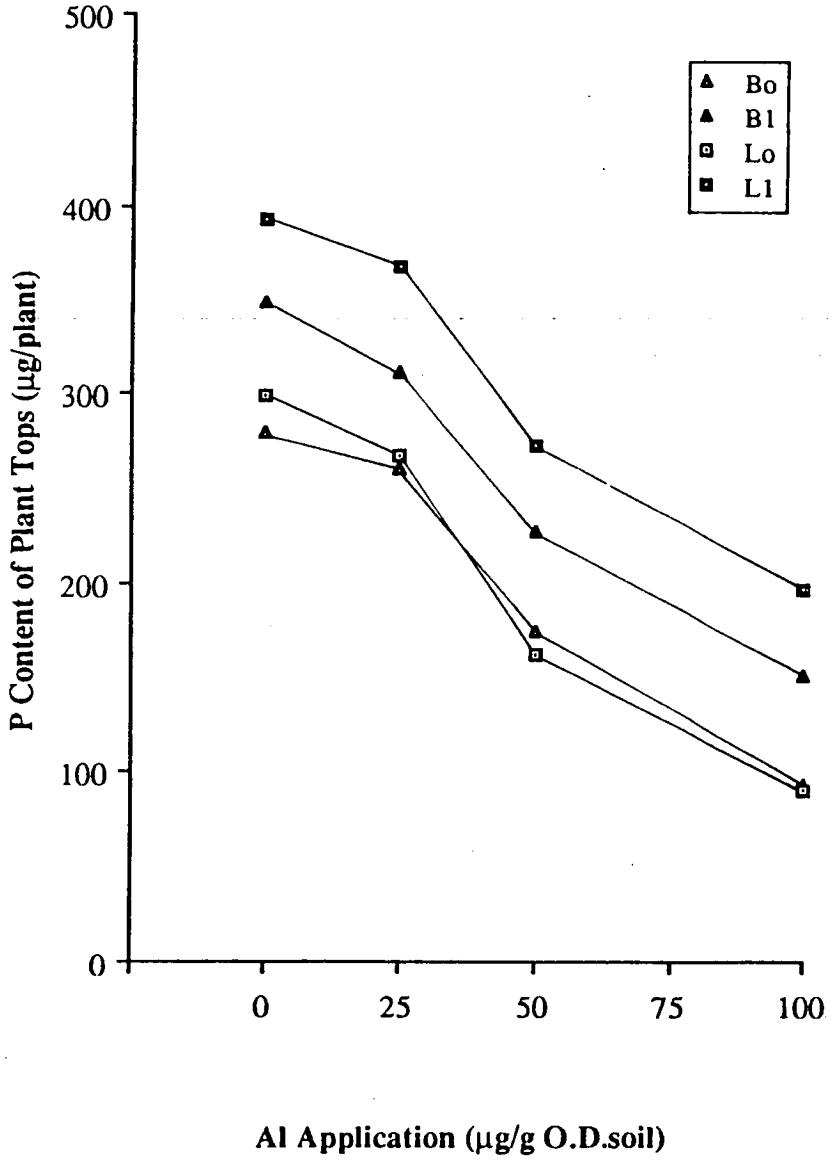


Figure 5.29 Relationship between phosphorus content of plant tops (µg/plant) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.22 Phosphorus content of plant tops ($\mu gP\ plant^{-1}$) in relation to type of organic matter, rate of organic matter and level of aluminium application. (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	314.11	285.85	200.56	122.21	230.68
Lucerne chaff	346.36	317.39	216.97	144.44	256.29
mean (A)	330.23	301.62	208.76	133.32	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 56.62 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	289.33	263.99	168.08	92.33	203.43
With O.M.	371.14	339.24	249.44	174.32	283.54

LSD (0.05); O.M. rate (R) = 16.75 *** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	201.74	259.62	230.68
Lucerne chaff	205.13	307.46	256.29

LSD (0.05); T x R = 23.69 *

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	279.18	260.37	174.31	93.12	349.04	311.33	226.81	151.31
Lucerne chaff	299.49	267.62	161.85	91.54	393.24	367.16	272.08	197.34

LSD (0.05); T x R x A = NS

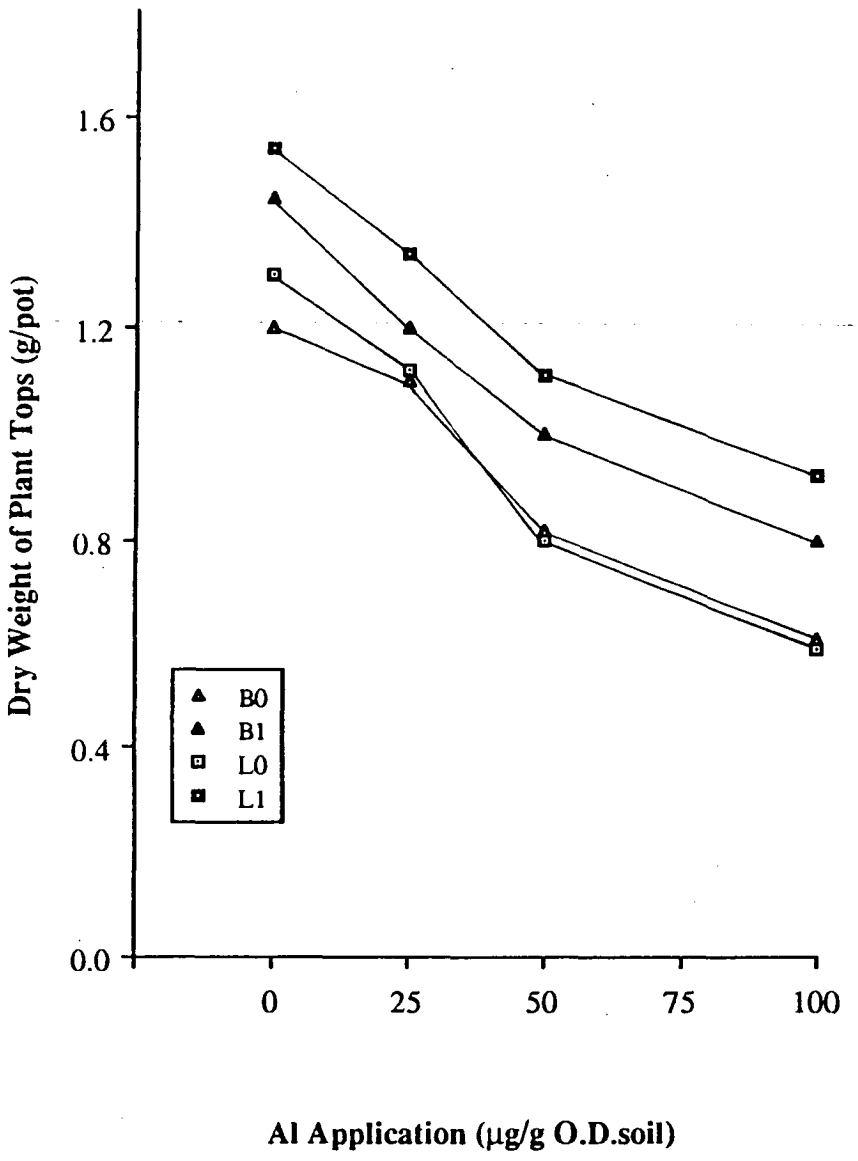


Figure 5.34 Relationship between dry weight of plant tops and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.23 Dry weight of plant tops (g pot^{-1}) in relation to type of organic matter, rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	1.33	1.15	0.91	0.71	1.02
Lucerne chaff	1.42	1.23	0.96	0.76	1.09
mean					
(A)	1.37	1.19	0.93	0.73	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.17 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	1.25	1.11	0.81	0.60	0.94
With O.M.	1.49	1.27	1.05	0.86	1.17

LSD (0.05); O.M. rate (R) = 0.13 ** R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	0.93	1.11	1.02
Lucerne chaff	0.95	1.23	1.09

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	1.20	1.10	0.82	0.61	1.45	1.20	1.00	0.80
Lucerne chaff	1.30	1.12	0.80	0.59	1.54	1.34	1.11	0.92

LSD (0.05); T x R x A = NS

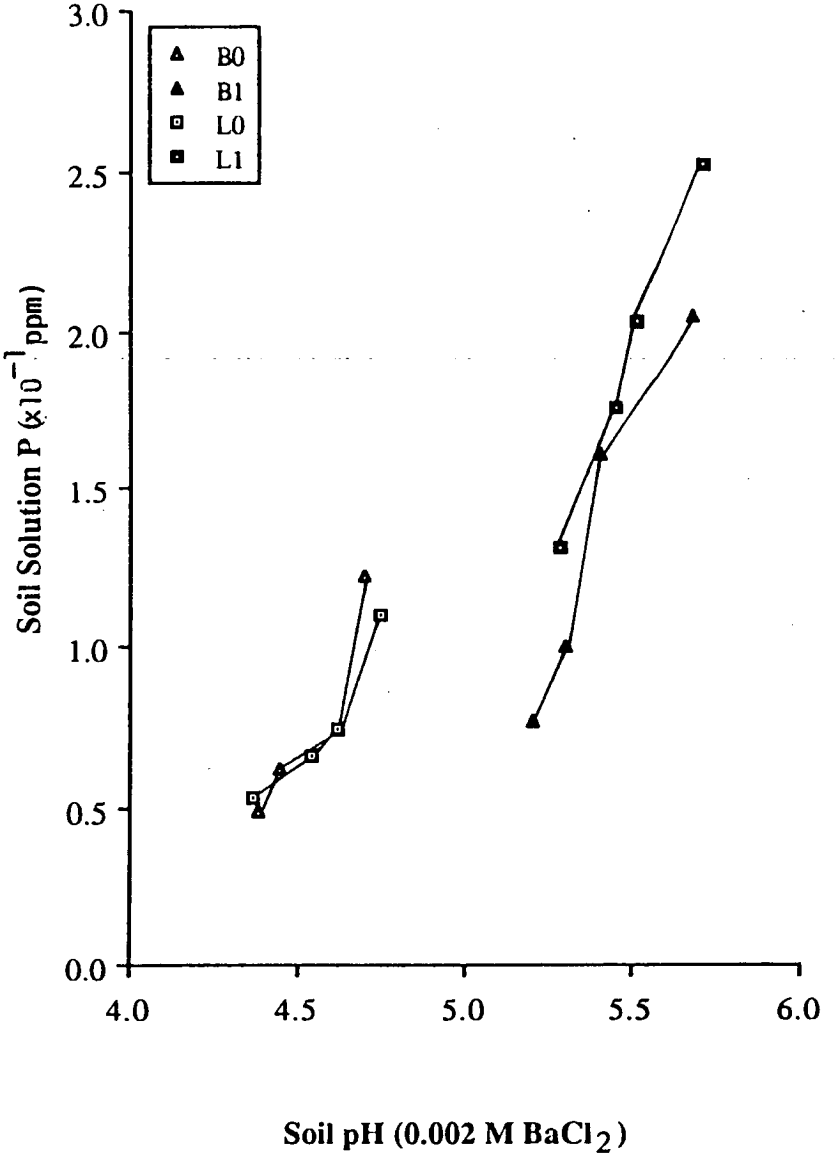


Figure 5.30 Relationship between soil solution phosphorus (ppm,pF2) and soil reaction with and without added organic matter as barley straw (B1, Bo) and lucerne chaff (L1, Lo).

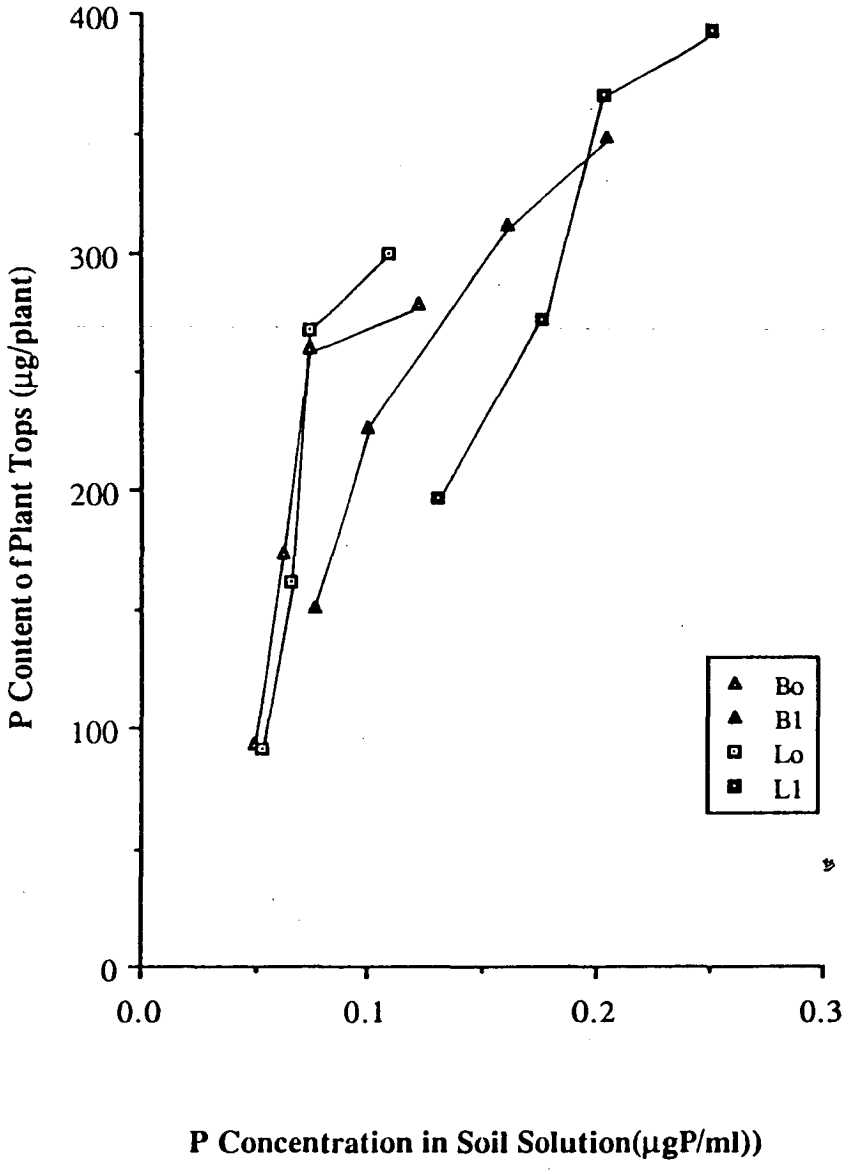


Figure 5.31 Relationship between phosphorus content of plant tops (µg/plant) and phosphorus concentration in soil solution (ppm,pF2) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

was between 0.2-0.25 ppm (Figure 5.32, 5.33, respectively). The results were in conformity with those obtained for Sequence (a).

Plant dry matter production: Yield of plant tops and roots decreased ($P<0.001$) with increased rate of aluminium application both with and without added organic matter (Figures 5.34, 5.35; Appendix 5.12). Yield of tops and roots were higher in the presence of added organic matter ($P<0.01$, $P<0.05$, respectively) at each level of application of aluminium (Tables 5.23, 5.24).

The highest yield of both plant tops and roots was obtained in response to organic matter added as lucerne chaff (Al-0 ppm; O.M.-L1). These yields were assigned a value of 100 and yields of other treatments were calculated as percentages (Figures 5.36, 5.37). The control treatments (Al-0 ppm; O.M.-Lo, Bo) yielded 80% and 90% respectively. However, at the highest rate of application of aluminium without added organic matter (Al-100 ppm; O.M.-Lo, Bo) yield was no more than 40% of that obtained with organic matter added as lucerne chaff. As with Sequence (a) plants, symptoms of aluminium toxicity were observed only in response to the highest rate of application of $Al_2(SO_4)3.14H_2O$ without added organic matter (Al-100 ppm; O.M.-Bo, Lo).

These results are consistent with those for Sequence (a) of the experiment. They emphasize further that active aluminium can be a critical growth-limiting factor. On the other hand added organic matter reduced aluminium toxicity very substantially, again at all levels of aluminium application.

5.4. Final Discussion and Conclusions

The effectiveness of organic matter under two conditions of incubation with excess aluminium (i.e., Sequence (a) and (b)) was compared using a technique of slope and intercept comparison based on Zar (1984) (Table 5.25).

Exchangeable and soil solution levels of aluminium were depressed after the addition of decomposable organic matter at all levels of application of soluble aluminium as $Al_2(SO_4)3.14H_2O$ in Burnie clay loam specimens subjected to both

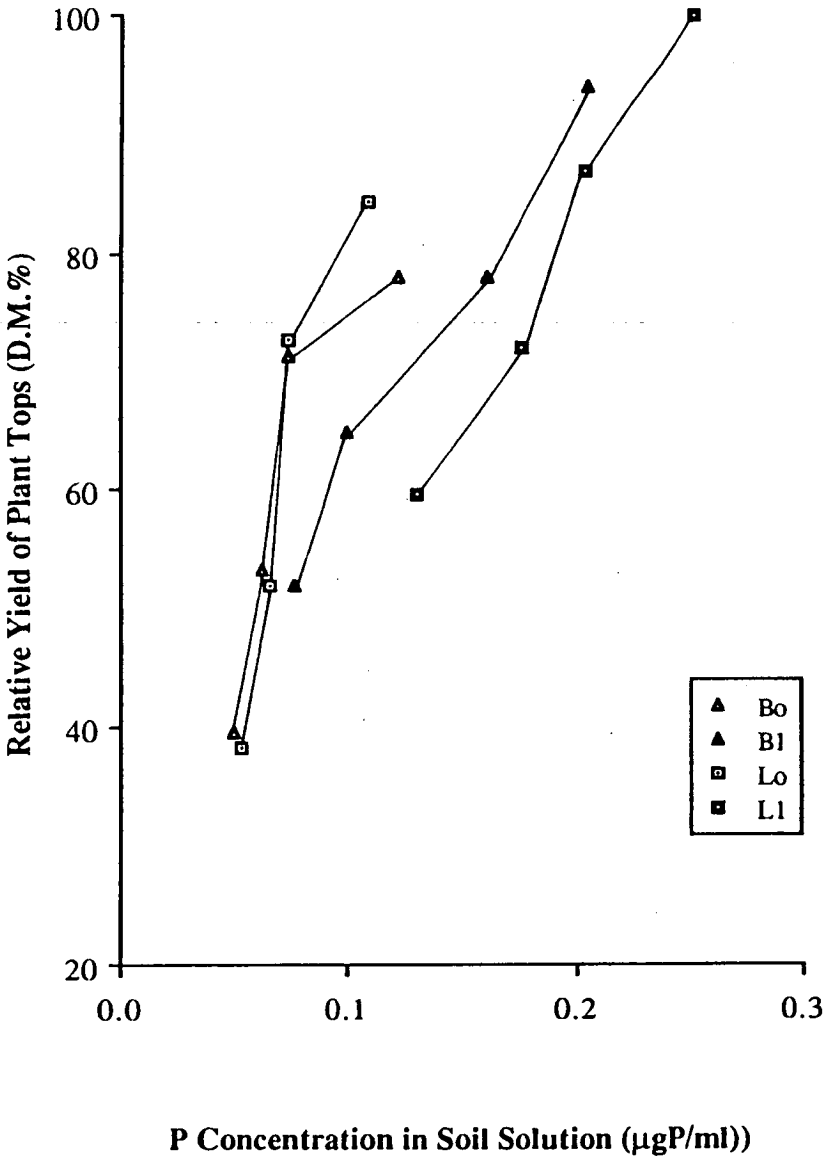


Figure 5.32 Relationship between relative yield of plant tops (D.M.%) and concentration of phosphorus in soil solution (ppm,pF2) with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).(Relative yield calculated as described on P. 139 above)

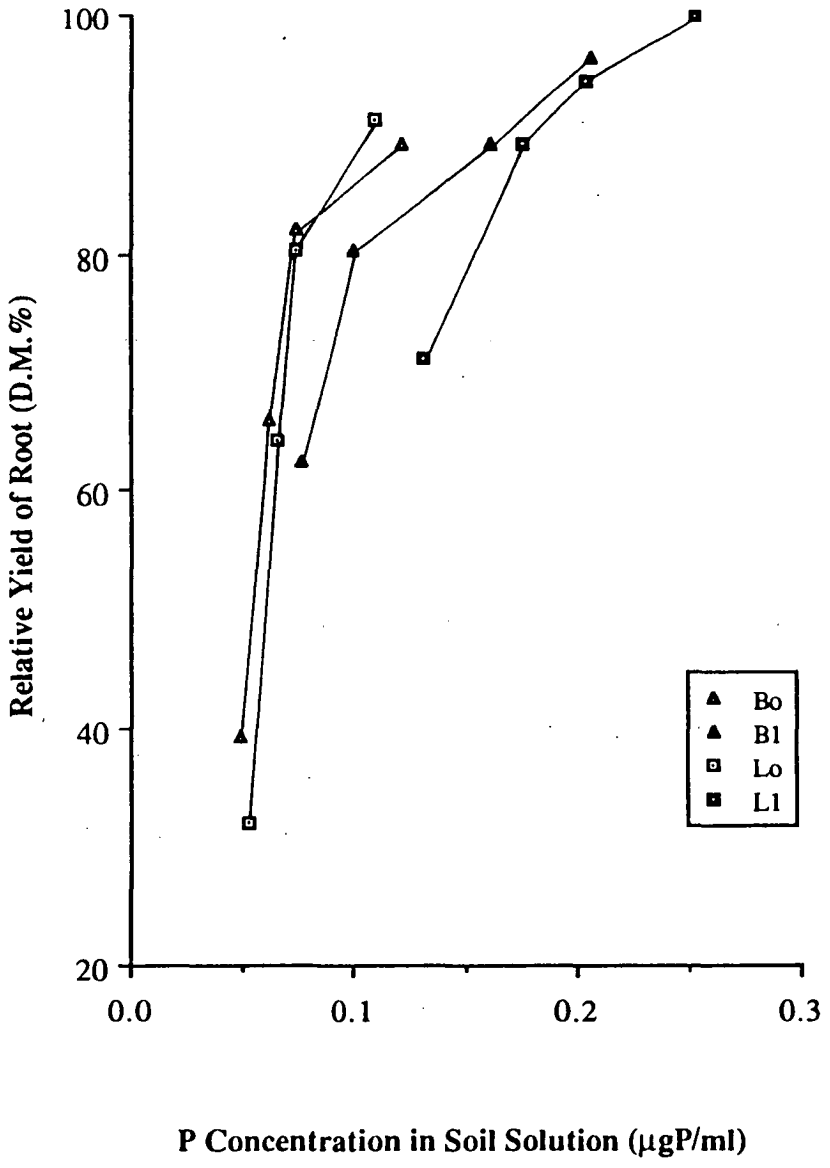


Figure 5.33 Relationship between relative yield of plant roots (D.M.%) and concentration of phosphorus in soil solution (ppm,pF2) with and without added organic matter as barley straw (Bl, Bo) or lucerne chaff (Ll, Lo).(Relative yield calculated as described on P, 139 above)

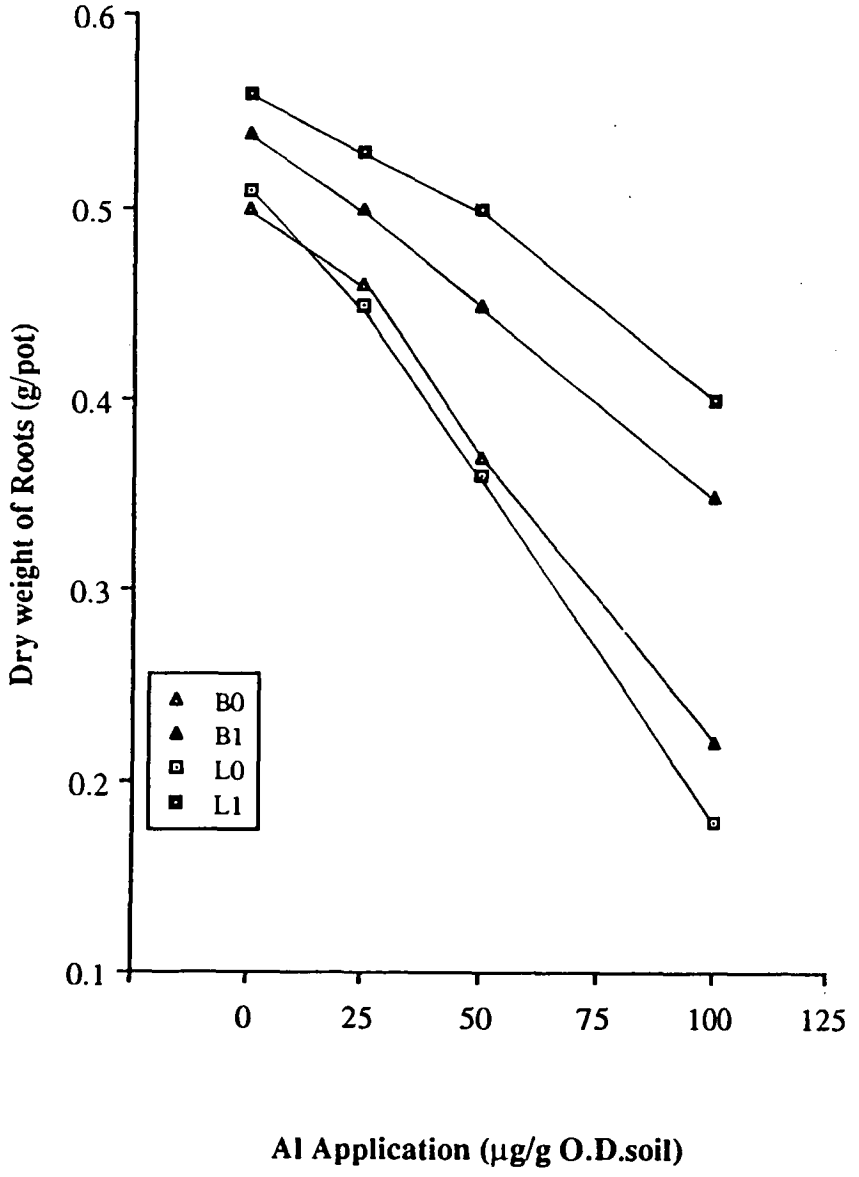


Figure 5.35 Relationship between dry weight of roots and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.24 Root dry weight (g pot^{-1}) in relation to type of organic matter, rate of organic matter and level of aluminium application (Means of three replicates)

i. Organic matter type (T) x Al application (A)

(A)	0	25	50	100	mean
O.M. type					
Barley straw	0.52	0.48	0.41	0.29	0.42
Lucerne chaff	0.54	0.49	0.43	0.29	0.44
mean (A)	0.53	0.48	0.42	0.29	

LSD (0.05); O.M. type (T) = NS T x A = NS
Al application (A) = 0.07 ***

ii. Organic matter rate (R) x Al applied (A)

(A)	0	25	50	100	mean
O.M. rate					
Without O.M.	0.50	0.45	0.36	0.20	0.38
With O.M.	0.55	0.51	0.47	0.37	0.48

LSD (0.05); O.M. rate (R) = 0.06 * R x A = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	0.39	0.46	0.42
Lucerne chaff	0.38	0.50	0.44

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x Al application

O.M. rate	Without O.M.				With O.M.			
Al application	0	25	50	100	0	25	50	100
O.M. type								
Barley straw	0.50	0.46	0.37	0.22	0.54	0.50	0.45	0.35
Lucerne chaff	0.51	0.45	0.36	0.18	0.56	0.53	0.50	0.40

LSD (0.05); T x R x A = NS

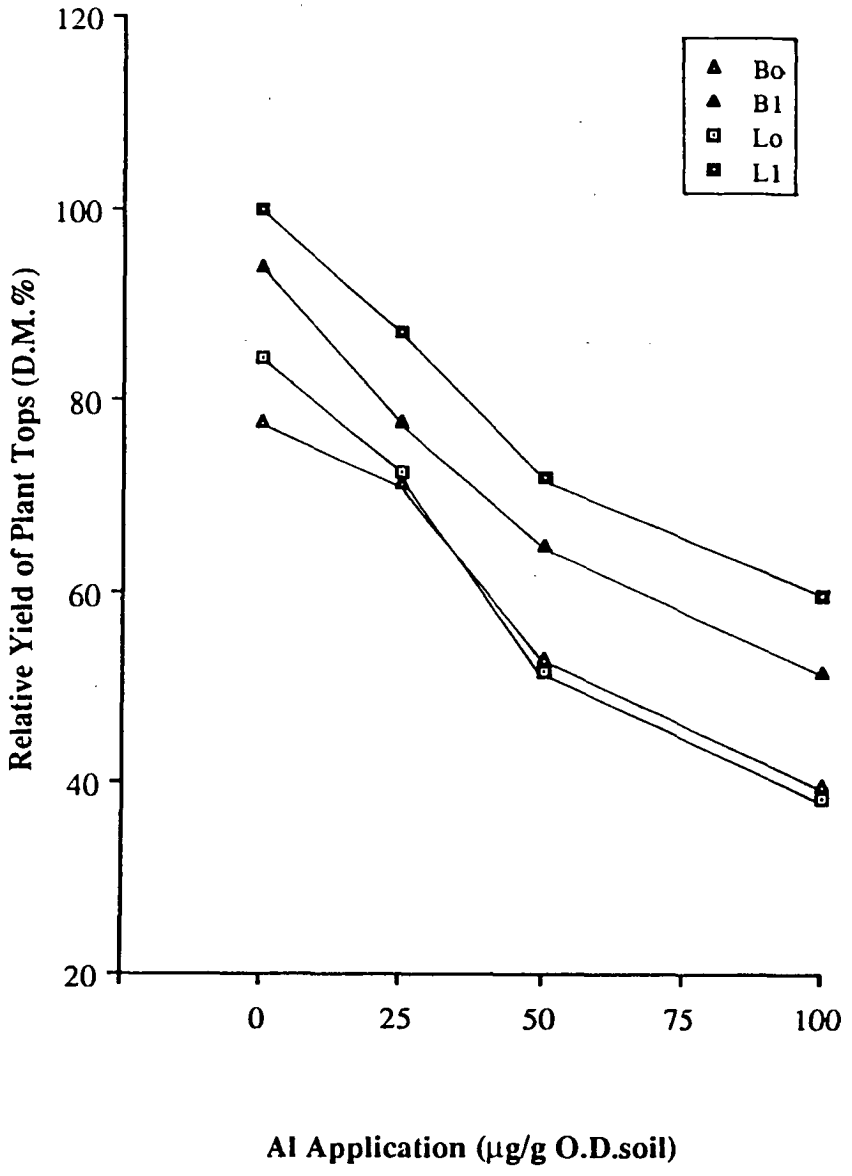


Figure 5.36 Relationship between relative yield of plant tops (D.M.%) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).(Relative yield calculated as described on P.94above).

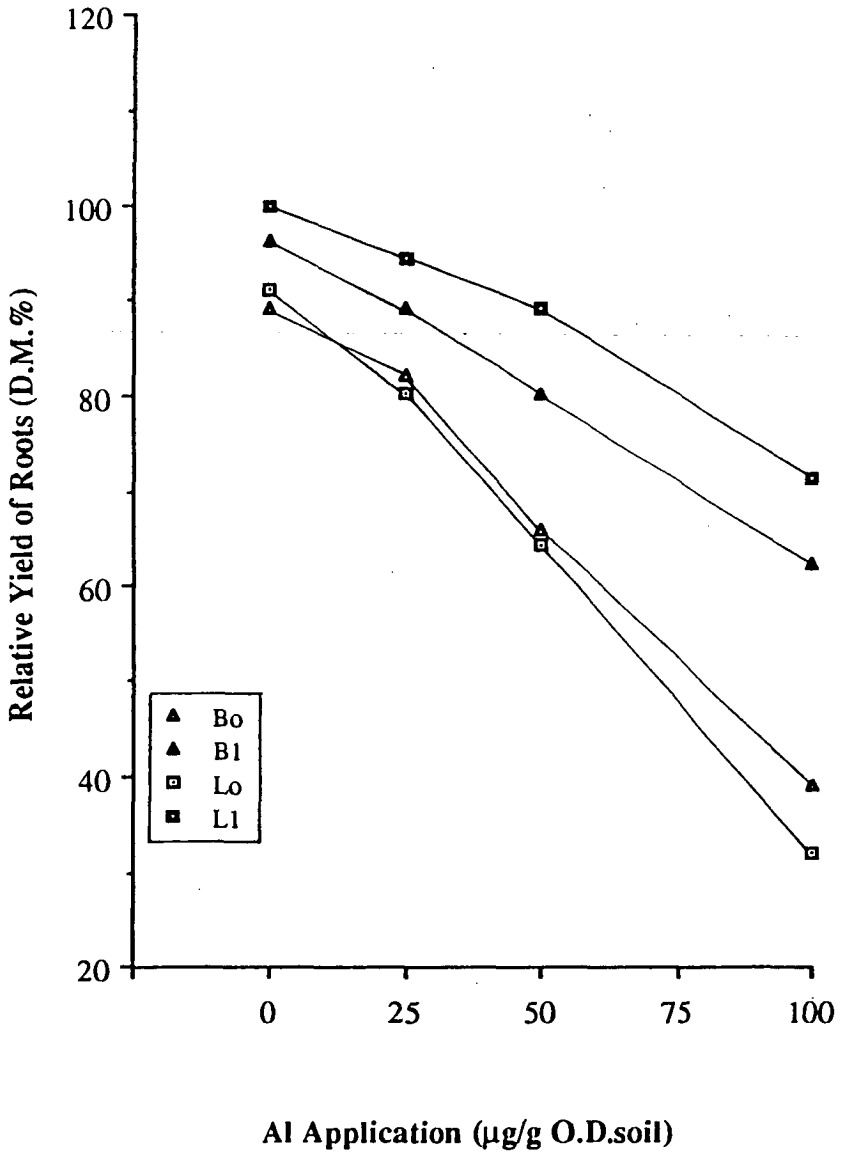


Figure 5.37 Relationship between relative yield of roots (D.M.%) and level of aluminium applied as $Al_2(SO_4)_3.14H_2O$ with and without added organic matter as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 5.25 Slope and intercept comparisons after Zar (1984) for effects of added organic matter and soluble aluminium on parameters measured under conditions of Sequence (a) and Sequence (b) for Burnie clay loam (0-15 cm)

Remarks : Slope and intercept comparisons made by method of Zar (1984) using t-value from table on df (2), 4 and (2), 5 for slope and intercept respectively.

B, L	=	barley straw or lucerne chaff added
R1, Ro	=	with and without organic matter
a, b	=	incubation sequence
SE	=	Standard error
r	=	Correlation coefficient
NS	=	not significant
*, **, ***	=	significant at 95, 99, 99.9% level respectively

			Slope	SE	Intercept	SE	r	P	t-value			
									Slope	P	Intercept	P
pH(soil)	B	(a)	-0.004	0.001	5.59	0.061	0.92	NS	0.426	NS	0.035	NS
		(b)	-0.004	0.001	5.588	0.081	0.91	NS				
	L	(a)	-0.004	0.001	5.782	0.045	0.97	<0.05	0.226	NS	0.108	NS
		(b)	-0.004	0.001	5.664	0.041	0.97	<0.05				
	Ro	(a)	-0.004	0.00026	4.83	0.021	0.99	<0.01	0.243	NS	0.12	NS
		(b)	-0.004	0.00043	4.704	0.025	0.99	<0.01				
	R1	(a)	-0.002	0.001	5.542	0.027	0.91	NS	1.707	NS	0.015	NS
		(b)	-0.004	0.001	5.62	0.061	0.94	NS				
Al	B	(a)	0.165	0.018	36.1	1.051	0.99	<0.01	5.933	**	–	
(1M KCl)		(b)	0.338	0.023	43.686	1.294	0.995	<0.01				
	L	(a)	0.076	0.017	21.452	0.966	0.95	<0.05	6.465	**	–	
		(b)	0.197	0.008	24.318	0.465	0.978	<0.01				
	Ro	(a)	0.668	0.102	109.13	5.848	0.98	<0.05	0.749	NS	18.325	***
		(b)	0.894	0.284	117.56	16.269	0.91	0.15				
	R1	(a)	0.121	0.007	28.778	0.396	0.996	<0.01	8.778	***	–	
		(b)	0.268	0.015	34.0	0.873	0.997	<0.01				

(Continue)

			Slope	SE	Intercept	SE	r	P	t-value			
									Slope	P	Intercept	P
Al	B	(a)	0.121	0.015	1.586	0.875	0.98	<0.01	0.244	NS	2.998	*
(monomeric)		(b)	0.131	0.038	4.172	2.156	0.93	NS				
	L	(a)	0.076	0.008	1.828	0.464	.99	<0.01	0.708	NS	2.645	*
		(b)	0.095	0.027	3.614	1.518	0.93	NS				
	Ro	(a)	0.379	0.018	3.56	1.022	0.998	<0.01	4.406	*		
		(b)	0.65	0.059	0.636	3.365	0.99	<0.01				
	R1	(a)	0.099	0.012	1.708	0.666	0.986	<0.01	0.432	NS	2.828	*
		(b)	0.113	0.032	3.89	1.837	0.93	NS				
P (HCO_3^-	B	(a)	-0.311	0.071	105.01	4.048	0.95	<0.05	0.107	NS	10.603	***
extractable)		(b)	-0.323	0.081	94.92	4.668	0.94	NS				
	L	(a)	-0.249	0.046	116.99	2.62	0.97	<0.05	0.411	NS	16.32	***
		(b)	-0.376	0.078	115.23	4.442	0.96	<0.05				
	Ro	(a)	-0.392	0.018	96.364	1.019	0.998	<0.01	0.12	NS	18.45	***
		(b)	-0.403	0.085	78.37	4.876	0.96	<0.05				
	R1	(a)	-0.28	0.057	111.0	3.254	0.96	<0.05	0.719	NS	8.96	***
		(b)	-0.349	0.078	105.07	4.452	0.95	<0.05				

(Continue)

			Slope	SE	Intercept	SE	r	P	t-value			
									Slope	P	Intercept	P
P in soil solution	B	(a)	-0.011	0.003	2.12	0.188	0.93	NS	0.299	NS	0.26	NS
		(b)	-0.013	0.003	1.92	0.184	0.94	NS				
	L	(a)	-0.011	0.003	2.32	0.162	0.94	NS	0.098	NS	0.08	NS
		(b)	-0.012	0.002	2.414	0.093	0.98	<0.05				
	Ro	(a)	-0.007	0.002	1.482	0.103	0.95	<0.05	0.581	NS	0.393	NS
		(b)	-0.006	0.002	1.018	0.123	0.89	NS				
	R1	(a)	-0.011	0.003	2.214	0.176	0.93	NS	0.226	NS	0.088	NS
		(b)	-0.012	0.002	2.164	0.128	0.97	<0.05				
P in plant	B	(a)	-4.072	1.899	2025.06	108.79	0.697	NS	0.363	NS	2.5	NS
		(b)	-5.003	1.724	2063.32	98.74	0.809	NS				
	L	(a)	-3.534	1.858	2127.86	106.42	0.644	NS	0.045	NS	0.875	NS
		(b)	-3.651	1.831	2132.12	104.89	0.665	NS				
	Ro	(a)	-6.631	1.659	1932.68	95.02	0.889	NS	0.083	NS	2.175	NS
		(b)	-6.825	1.632	1939.04	93.50	0.897	NS				
	R1	(a)	-4.245	1.806	2096.38	103.46	0.734	NS	0.033	NS	2.275	NS
		(b)	-4.327	1.777	2097.72	101.78	0.748	NS				

(Continue)

			Slope	SE	Intercept	SE	r	P	t-value			
									Slope	P	Intercept	P
Shoot dry weight	B	(a)	-0.006	0.0004	1.952	0.02	0.996	<0.01	0.425	NS	0.583	NS
		(b)	-0.006	0.001	1.39	0.06	0.97	<0.05				
	L	(a)	-0.005	0.001	2.036	0.031	0.989	<0.05	0.936	NS	0.583	NS
		(b)	-0.006	0.001	1.498	0.054	0.978	<0.05				
	Ro	(a)	-0.01	0.002	1.86	0.087	0.979	<0.05	1.98	NS	0.465	NS
		(b)	-0.007	0.001	1.236	0.058	0.978	<0.05				
	R1	(a)	-0.006	0.0004	1.994	0.023	0.995	<0.01	0.558	NS	0.585	NS
		(b)	-0.006	0.001	1.434	0.054	0.977	<0.05				
Root dry weight	B	(a)	-0.002	0.0003	0.662	0.018	0.98	<0.05	1.289	NS	0.10	NS
		(b)	-0.002	0.0001	0.544	0.003	0.999	<0.001				
	L	(a)	-0.002	0.0001	0.698	0.005	0.998	<0.01	2.164	NS	0.113	NS
		(b)	-0.002	0.0002	0.568	0.009	0.99	<0.01				
	Ro	(a)	-0.003	0.0001	0.596	0.005	0.999	<0.001	0.688	NS	0.078	NS
		(b)	-0.003	0.0002	0.512	0.011	0.996	<0.01				
	R1	(a)	-0.002	0.0002	0.678	0.011	0.992	<0.01	1.745	NS	0.108	NS
		(b)	-0.002	0.0001	0.554	0.005	0.998	<0.01				

Sequence (a) and (b). However, the effects of added organic matter were greater ($P<0.01$, 0.01, 0.001, 0.001) in Sequence (a) soil plus organic matter mixtures for both types of organic matter. Most significantly monomeric aluminium in the soil solution at pF2 was reduced more ($P<0.05$) under Sequence (a) conditions than under those of Sequence (b). Conversely available phosphorus was higher ($P<0.001$) in Sequence (a) soils than in Sequence (b) for the same treatment combinations.

Differences between Sequence (a) and Sequence (b) in the effects of type and rate of added organic matter on soil pH, phosphorus concentration in the soil solution (pF2), phosphorus uptake by the test plant and shoot and root dry weights were not significant ($P>0.05$) although as emphasized added organic matter had marked effects on these parameters within each sequence.

Thus any form of decomposable organic matter whether fresh or partly decomposed may be expected to have beneficial effects in suppressing active aluminium and enhancing plant growth in acid soils where aluminium is present as an exchangeable ion or in the soil solution. These effects were observed in Burnie clay loam in spite of its long history of addition of phosphorus as superphosphate.

6. SOME EFFECTS OF ADDED ORGANIC MATTER AND PHOSPHORUS FERTILIZER ON SOIL ALUMINIUM IN RELATION TO PLANT GROWTH.

6.1. Introduction

In most strongly acidic soils, aluminium toxicity is an important factor in reduced crop production especially in those soils that are low in phosphate. In such soils fertilizer phosphorus may be rapidly converted to insoluble forms.

Liming has long been a conventional practice for reducing soil acidity (Cassel, 1980) and the level of active aluminium (Evans and Kamprath, 1970; Farina et al 1980). More recently it has been shown that liming may cause adverse effects on the growth of maize as pH approaches neutrality due to reduction of available phosphorus, zinc, boron and manganese (Farina et al., 1980) and generally by reducing plant uptake of magnesium (Pavan et al., 1984).

Only small amounts of soluble aluminium have been detected in soils high in organic matter (Evans and Kamprath, 1970). Sorption of phosphorus is less when both inorganic (Adams and Pearson, 1967) and organic (Deb and Datta, 1967; Nagarajah et al., 1970) anions compete with phosphorus for sorption sites. Finally, a number of workers have shown that organic matter applied to strongly acid soils could reduce levels of active aluminium (Brogan, 1967; Hoyt and Turner, 1975).

Thus application of organic matter may be a feasible alternative to liming where aluminium toxicity is the main consequence of strong soil acidity. However there is little information in the literature to support the claim that added organic matter can both reduce aluminium toxicity and enhance the availability of phosphorus from phosphate fertilizer in acidic soils. Therefore the present experiment was designed to evaluate such effects in a strongly acid krasnozem from North-Western Tasmania.

6.2. Materials and Methods

6.2.1. Experimental design

The variables in this experiment were

Variable (1): two types of organic matter, viz., barley straw and lucerne chaff.

Variable (2): two rates of organic matter, viz., nil added organic matter and organic matter added at the rate of 80 g./kg of soil (O.D.), i.e., 96 g/pot.

Variable (3): four rates of fertilizer phosphorus as potassium orthophosphate (KH_2PO_4, A.R. grade) viz., 0, 100, 200, 400 µg P/g soil (O.D.).

The treatments were arranged in a split-split plot design with 3 replications in a glasshouse under the same conditions as before.

6.2.2. Soil and organic materials

Soil used was the surface 15 cm (A horizon) of Lapoinya clay loam an acid krasnozem developed on basalt on the northern edge of the Central Plateau North-Western Tasmania (Loveday and Farquhar, 1958). The soil was collected at the Elliott Research Station of the Tasmanian Department of Agriculture from the "museum" soil area to which no fertilizer has been applied for many years. Some properties of this soil are given in Table 3.1. It was selected for this experiment because of its low pH, very low phosphorus concentration, and high level of active aluminium.

The same two kinds of organic matter were used as in the earlier experiments. Their preparation and addition to the soil has been described in Chapter 2. The soil and soil plus organic matter were incubated for four weeks as described in Chapter 3 before addition of fertilizer phosphorus in the same manner as that described for addition of aluminium sulphate in Chapter 5 section 5.2.3. Basal nutrients were applied as for the previous experiment (Chapter 5).

6.2.3. Plant growth, harvest, and preparation of plant material for analysis

These procedures were the same as those described for the previous experiment (Chapter 5 section 5.2.4)

6.2.4. Chemical analysis of plant materials

Phosphorus was determined as described in Chapter 5 section 5.2.5 .

6.2.5. Chemical analysis of soil materials

The pot contents were sampled after harvest of plant materials and specimens were prepared for analysis as before (Chapter 5 section 5.2.6). Soil reaction (pH), ionic strength of soil solution, exchangeable aluminium, available phosphorus, and composition of soil solution (phosphorus, inorganic monomeric and organically-complexed aluminium, and total aluminium) were all determined as described in Chapter 5 section 5.2.6 and 5.2.7.

6.3. Results and Discussion

6.3.1. Aluminium

Exchangeable aluminium decreased ($P<0.01$) with increasing rate of application of phosphorus as KH_2PO_4 (Figure 6.1; Table 6.1; Appendix 6.1). This is in agreement with the results of Munns (1965) and Hsu (1965). They showed that addition of soluble phosphate in sufficient quantities to both nutrient solutions and acid soils decreased levels of aluminium in solution either by precipitation or adsorption. In the present work the overall effect was much greater ($P<0.001$) in the presence of added organic matter.When exchangeable aluminium was plotted against soil reaction (pH 0.002 M $BaCl_2$) there was a clear separation of the data in relation to presence or absence of added organic matter (Figure 6.2)

Both total aluminium and organically complexed aluminium increased ($P<0.001$) with rate of soluble phosphate application. The effect was also greater in the presence of added organic matter ($P<0.01$). The data show that nearly all of the aluminium in soil solution was in the organically-complexed form (Figure 6.3 (a, b); Table 6.2, 6.3; Appendix 6.2). The rate of increase of soil solution aluminium, both

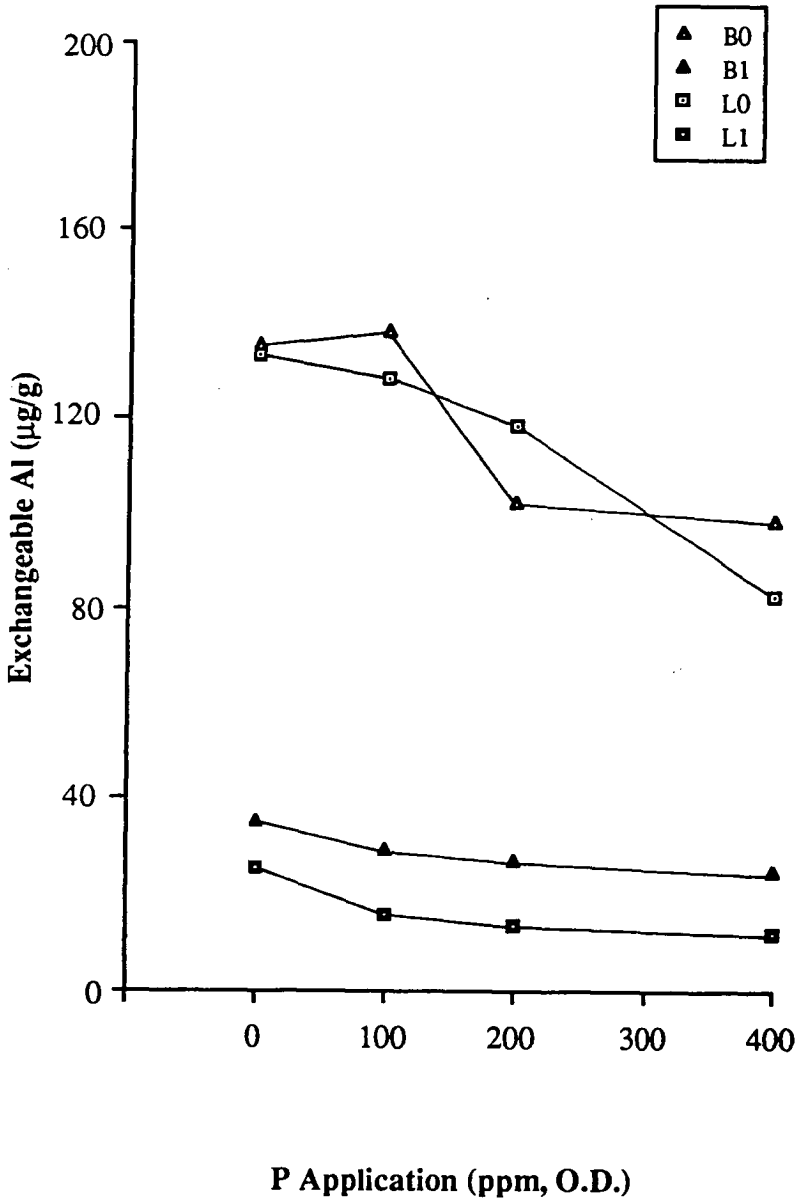


Figure 6.1 Effect of rate of phosphate application on exchangeable aluminium with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.1 Exchangeable aluminium (μg/g) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	86.06	84.81	65.44	62.47	74.69
Lucerne chaff	80.32	72.75	66.74	47.95	66.94
mean (P)	83.19	78.78	66.09	55.21	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 16.11 **

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	135.49	134.58	111.65	91.88	118.4
With O.M.	30.89	22.98	20.52	18.54	23.23

LSD (0.05); O.M. rate (R) = 15.46 *** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	119.84	29.55	74.69
Lucerne chaff	116.96	16.92	66.94

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	136.45	139.62	103.51	99.78	35.67	29.99	27.36	25.16
Lucerne chaff	134.54	129.54	119.79	83.98	26.11	15.97	13.68	11.92

LSD (0.05); T x R x P = NS

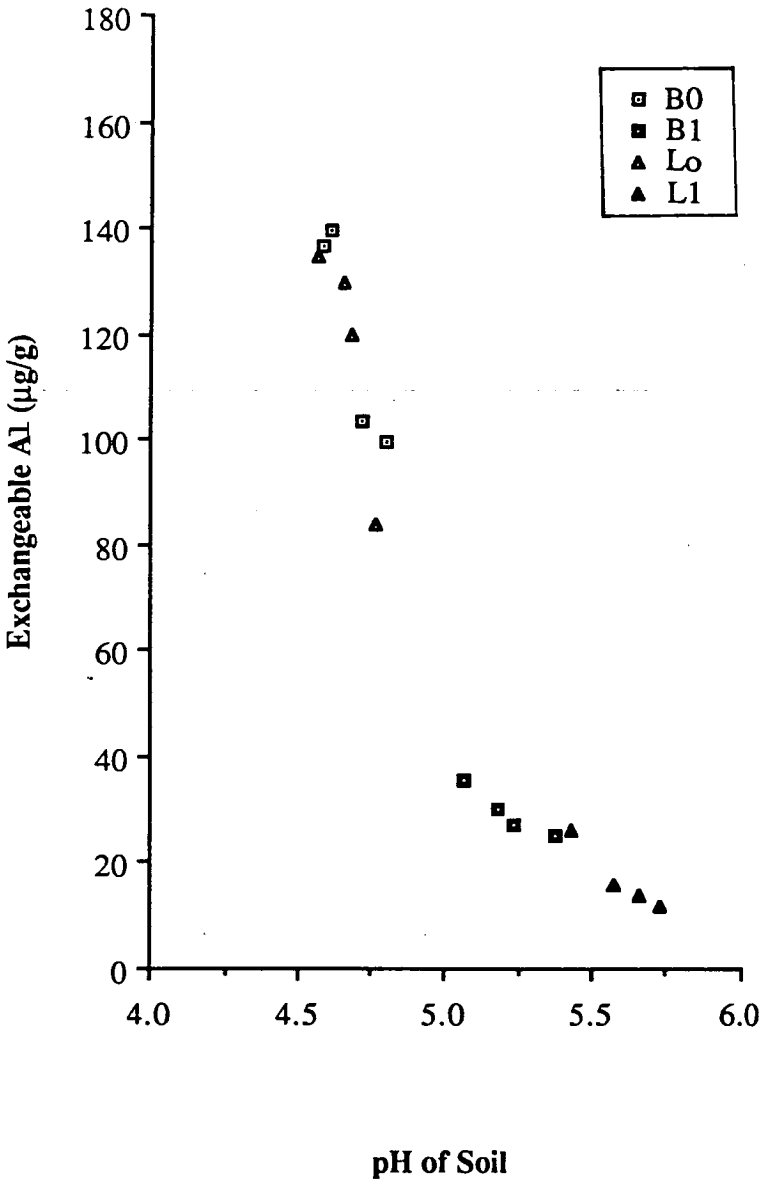
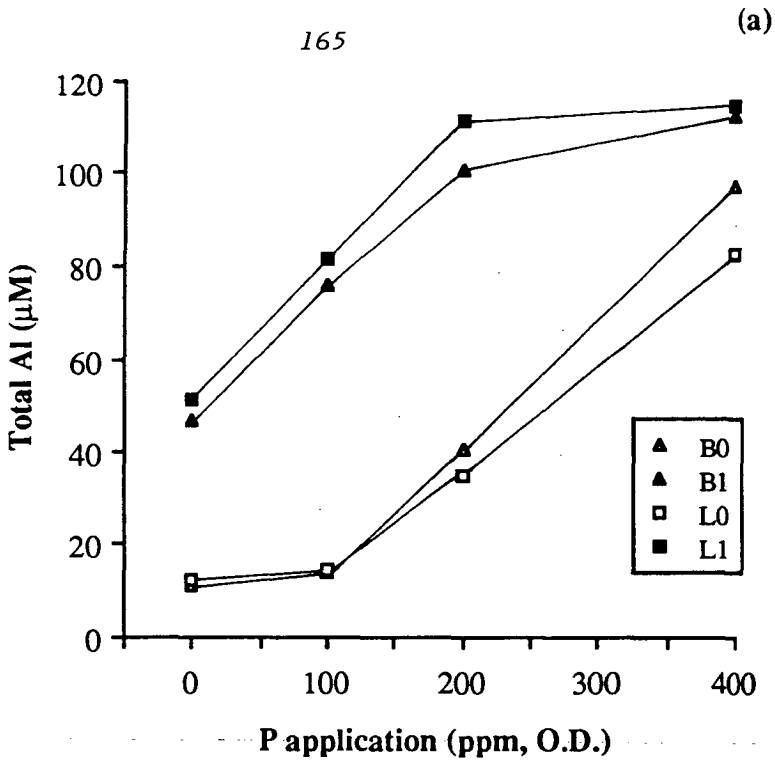


Figure 6.2 Relationship between soil reaction (pH 0.002 M $BaCl_2$) and exchangeable aluminium with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).



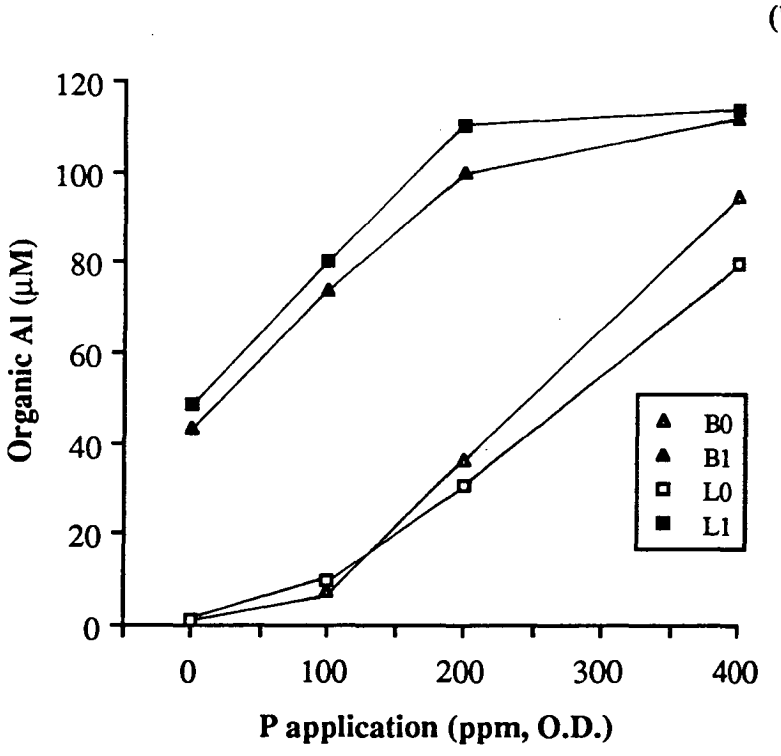


Figure 6.3 Effect of rate of phosphate application on (a) total aluminium and (b) organic aluminium in soil solution with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.2 Total aluminium in soil solution (μM) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	28.91	45.02	70.77	105.17	62.46
Lucerne chaff	31.81	48.31	73.38	98.87	63.09
mean (P)	30.36	46.66	72.07	102.02	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 9.65 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	11.87	14.43	37.81	90.22	38.58
With O.M.	48.85	78.88	106.33	113.82	86.97

LSD (0.05); O.M. rate (R) = 11.42 *** R x P = 10.45 ***

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	40.78	84.15	62.46
Lucerne chaff	36.39	89.80	63.09

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	11.32	13.95	40.46	97.41	46.50	76.08	101.07	112.94
Lucerne chaff	12.42	14.92	35.16	83.04	51.20	81.69	111.59	114.70

LSD (0.05); T x R x P = NS

Table 6.3 Organic aluminium in soil solution (μM) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	22.28	40.79	68.03	103.05	58.53
Lucerne chaff	24.82	44.93	70.38	96.68	59.2
mean (P)	23.55	42.86	69.20	99.86	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 10.20 **

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	1.05	8.67	33.46	87.03	32.56
With O.M.	46.03	77.04	104.94	112.68	85.17

LSD (0.05); O.M. rate (R) = 12.50 ** R x P = 10.09 *

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	34.89	82.18	58.53
Lucerne chaff	30.23	88.17	59.20

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	1.00	7.72	36.44	94.38	43.54	73.86	99.62	111.71
Lucerne chaff	1.10	9.63	30.49	79.69	48.53	80.22	110.27	113.66

LSD (0.05); T x R x P = NS

total and organic forms, was at first much greater in the presence of added organic matter, with only slight differences in relation to type of organic matter.

This difference in rate of increase of soil solution aluminium was reduced between 100 and 200 ppm of added phosphorus and reversed between 200 and 400 ppm. At the same time the rate of increase in the presence of added organic matter was greatly reduced while without added organic matter there was an increased rate of increase. Thus at the highest rate of phosphorus application the differences in levels of soluble aluminium were much reduced. Superficially it would seem that in the soils without added organic matter, the higher rates of phosphorus application may have affected the activity of native organic matter in respect of aluminium while the effect of added organic matter was, at the same time, approaching a plateau. It would be interesting to pursue the course of these phenomena over a longer period of time.

Just why there should be such an effect of rate of added soluble phosphate in the first place, especially in the absence of added organic matter, is unclear since it might have been predicted from solubility product considerations that soluble aluminium and phosphate should have combined to form insoluble aluminium phosphate complexes in this strongly acidic soil thus reducing the level of soluble aluminium, at least in the absence of added organic matter. With added organic matter it is at least feasible that its affinity for aluminium may have inhibited reaction between aluminium and phosphate especially when it is seen that the reaction of the soil plus organic matter mixture was always above pH (0.002 M $BaCl_2$) 5.0 (Figure 6.2).

In contrast, the concentration of monomeric aluminium in the soil solution decreased ($P<0.01$) with rate of soluble phosphate application (Figure 6.4; Table 6.4; Appendix 6.1). The effects with and without added organic matter showed the same overall trend of reducing monomeric aluminium concentration but at very different rates. An initial effect of added organic matter is again very clear with monomeric aluminium concentrations only about one fourth of those in the absence of added organic matter. Although differences between lucerne chaff and barley straw

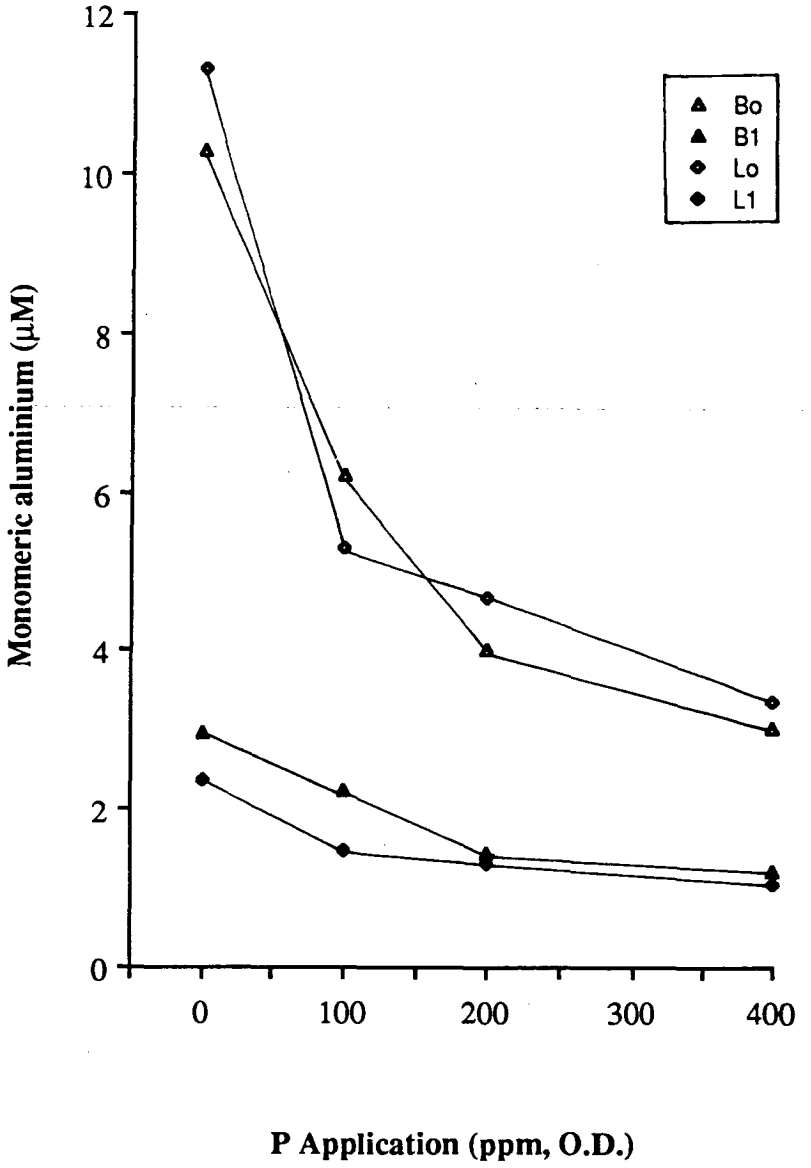


Figure 6.4 Effect of rate of phosphate application on monomeric aluminium in soil solution with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.4 Monomeric aluminium in soil solution (μM) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	6.63	4.22	2.74	2.13	3.93
Lucerne chaff	7.00	3.38	3.00	2.20	3.89
mean (P)	6.81	3.80	2.87	2.16	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 2.54 **

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	10.81	5.76	4.34	3.19	6.03
With O.M.	2.81	1.84	1.38	1.13	1.79

LSD (0.05); O.M. rate (R) = 2.0 ** R x P = 2.74 *

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	5.90	1.96	3.93
Lucerne chaff	6.16	1.63	3.89

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	10.31	6.23	4.02	3.03	2.96	2.22	1.45	1.23
Lucerne chaff	11.32	5.29	4.67	3.35	2.67	1.47	1.32	1.04

LSD (0.05); T x R x P = NS

were small and not statistically significant, lucerne chaff had a slightly greater and more immediate effect than barley straw up to 100 ppm of added phosphate with much smaller reductions in concentration of monomeric aluminium at 200 and 400 ppm. In the case of barley straw the effect was linear up to 200 ppm added phosphorus with a reduced effect between 200 and 400 ppm so that the curves for barley straw and lucerne chaff were then almost parallel.

In the absence of added organic matter there was a large reduction in concentration of monomeric aluminium (about 50%) from 0 to 100 ppm added phosphate in sharp contrast with the situation with added organic matter. Thereafter the concentration of monomeric aluminium continued to decrease at a rate much greater than was measured with added organic matter but at all levels of added phosphate the monomeric aluminium concentration was much greater without than with added organic matter. The major effect again may be attributed to organic matter, probably due to formation of organo-Al complexes and/or chelates or other complex interactions (Mortenson, 1963; Bartlett and Riego, 1972; Cabrera and Talibudeen, 1977). On the other hand the reduction in monomeric aluminium concentration with increasing amounts of added phosphate would seem, in this case, to be readily explained as due to formation of insoluble precipitates with phosphate.

6.3.2. Soil reaction and soil solution pH

The levels of exchangeable aluminium and of monomeric aluminium in the soil solution (pF2 extract) were closely related to soil reaction and the pH of the soil solution regardless of rate of phosphate application (Figure 6.2, 6.5). Application of organic matter increased pH ($P<0.01$) in both soil and soil solution. There were only small increases in soil reaction with rate of phosphate application but increases in soil solution pH in response to added OM were much greater ($P<0.001$) (Figure 6.6, 6.7; Table 6.5, 6.6; Appendix 6.3). Also lucerne chaff had a significantly greater ($P<0.05$) effect on soil reaction than barley straw. However, the difference was much less marked in respect of soil solution pH. The marked influence of organic matter on pH of soil and soil solution could be due to the mechanism of decomposition of

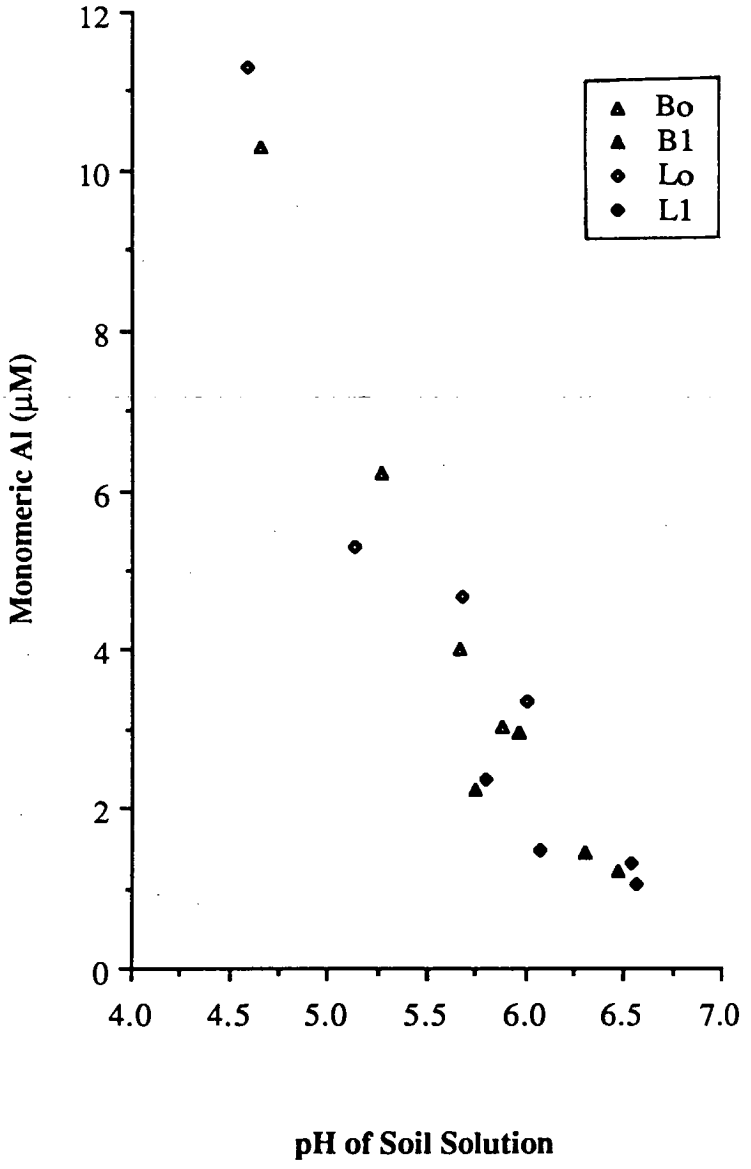


Figure 6.5 Relationship between pH of soil solution and monomeric aluminium with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

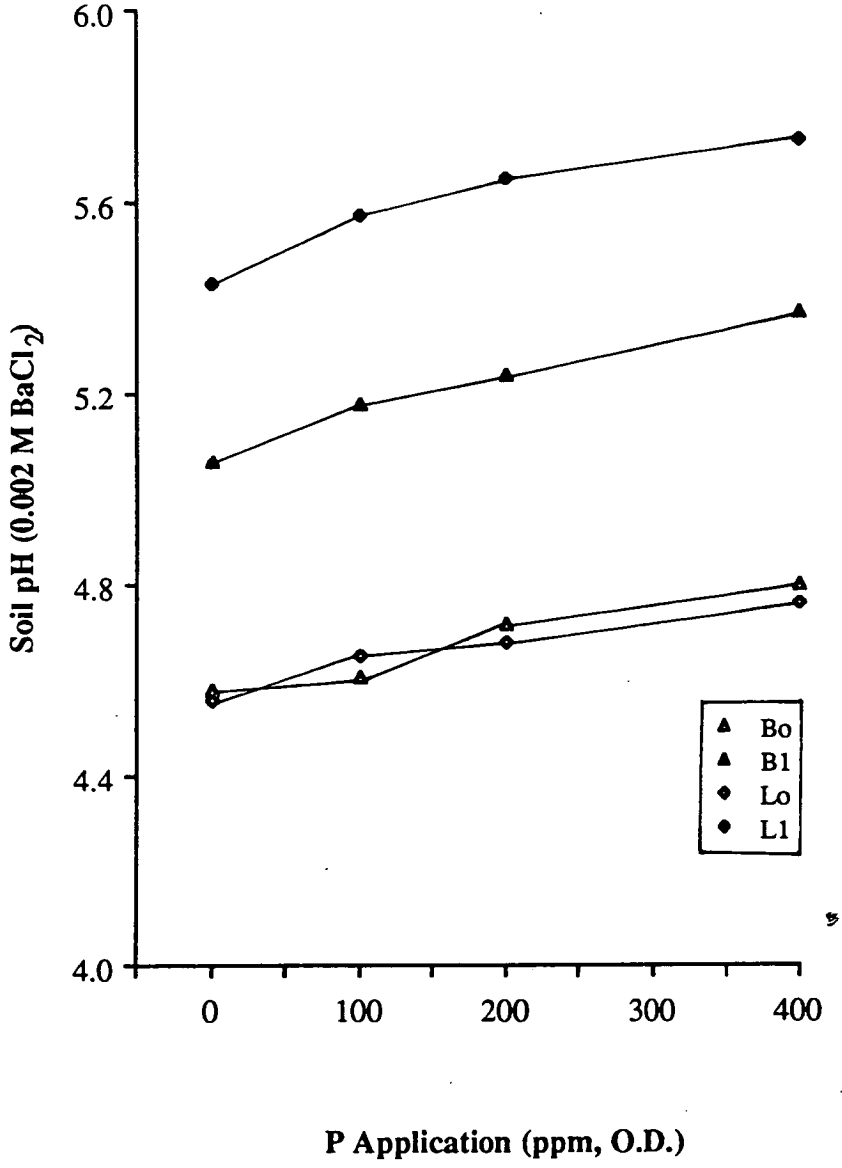


Figure 6.6 Effect of rate of phosphate application on soil reaction (pH 0.002 M $BaCl_2$) with and without organic matter added as barley straw (B1,.Bo) or lucerne chaff(L1, Lo).

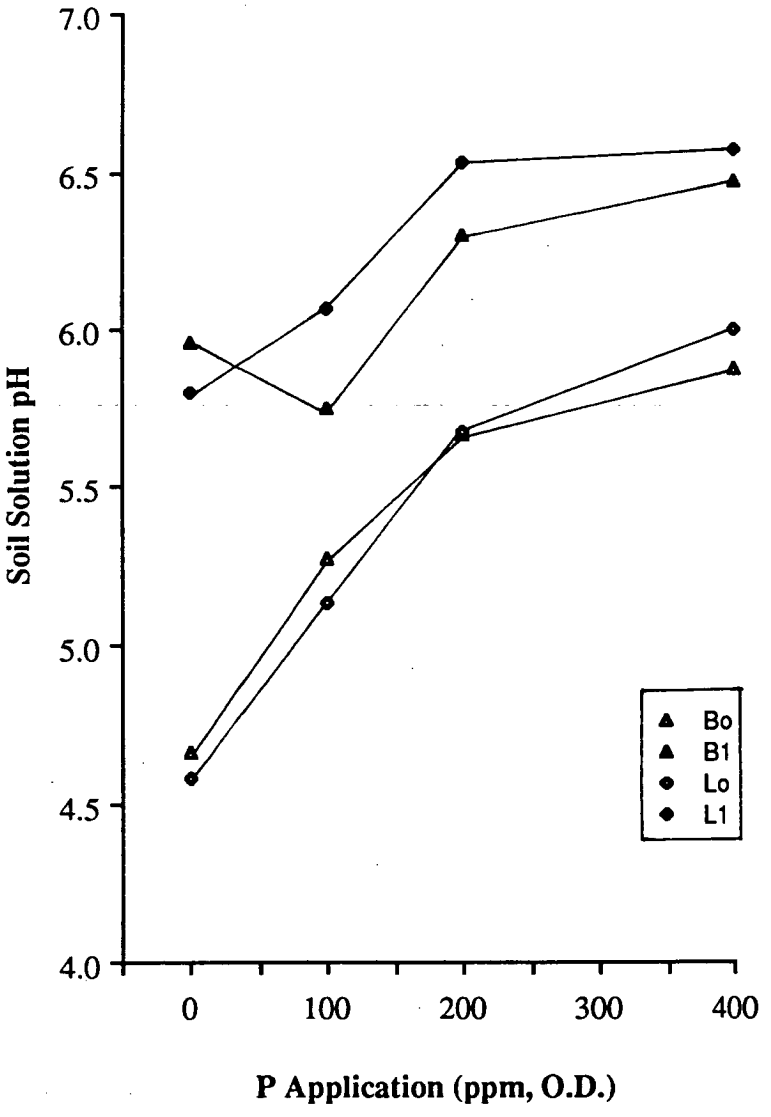


Figure 6.7 Effect of rate of phosphate application on soil solution pH with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1,.Lo).

Table 6.5 Soil reaction (pH 0.002 M $BaCl_2$) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	4.82	4.89	4.98	5.08	4.94
Lucerne chaff	5.0	5.11	5.17	5.25	5.13
mean (P)	4.91	5.0	5.07	5.17	

LSD (0.05); O.M. type (T) = 0.16 * T x P = NS
P application (P) = NS

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	4.57	4.63	4.70	4.78	4.67
With O.M.	5.24	5.37	5.44	5.55	5.40

LSD (0.05); O.M. rate (R) = 0.27 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	4.68	5.21	4.94
Lucerne chaff	4.66	5.60	5.13

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	4.58	4.61	4.72	4.80	5.06	5.18	5.24	5.37
Lucerne chaff	4.56	4.65	4.68	4.76	5.43	5.57	5.65	5.73

LSD (0.05); T x R x P = NS

Table 6.6 Soil solution pH in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	5.31	5.51	5.99	6.18	5.75
Lucerne chaff	5.19	5.60	6.11	6.29	5.80
mean (P)	5.25	5.56	6.05	6.24	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 0.4 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	4.62	5.20	5.67	5.94	5.36
With O.M.	5.88	5.91	6.41	6.52	6.18

LSD (0.05); O.M. rate (R) = 0.23 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	5.37	6.12	5.75
Lucerne chaff	5.35	6.24	5.80

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	4.66	5.27	5.67	5.88	5.96	5.75	6.30	6.47
Lucerne chaff	4.58	5.13	5.68	6.00	5.80	6.07	6.53	6.57

PπLSD (0.05); T x R x P = NS

organic matter as illustrated by Ritchie and Dolling (1985). They also reported that with maintenance of soil moisture at field capacity such pH changes could be due to the release of more organic anions with time.

The pH effects measured in the present study were similar to those recorded by Awad et al. (1976) and by Bloom (1981). Part of the effects may be attributed to reaction of phosphate with exchangeable and soil solution aluminium involving chemisorption and/or precipitation, in both cases reducing the hydrolysis of aluminium with consequent increase in pH of the soil solution.

The greater effect of organic matter in increasing soil and soil solution pH may also be due to complexing with aluminium and is clearly an important factor in reducing the concentration of active aluminium.

6.3.3. Ionic strength of soil solution

It is well known that the level and activity of monomeric aluminium are considerably influenced by ionic strength (Blamey et al., 1983; Alva et al., 1986a; and Kim et al., 1987). In the present study, the ionic strength of soil solution was affected ($P<0.001$) by addition of organic matter (Figure 6.8; Table 6.7; Appendix 6.3). Lucerne chaff had a greater effect ($P<0.01$) in increasing ionic strength than barley straw.

There was no significant effect on soil solution ionic strength at any rate of applied phosphate. However the trends shown in Figure 6.8 are interesting in that (1) effects with and without added organic matter are divergent with increasing rate of phosphorus application, and (2) ionic strength with added lucerne chaff is consistently higher than for barley straw. These effects may be associated with appreciable amounts of cations released from the organic materials over the period of incubation (Gillman and Bell, 1978) with more being released after addition of lucerne chaff than after barley straw. Clearly, little of the added phosphate remained in solution after six weeks.

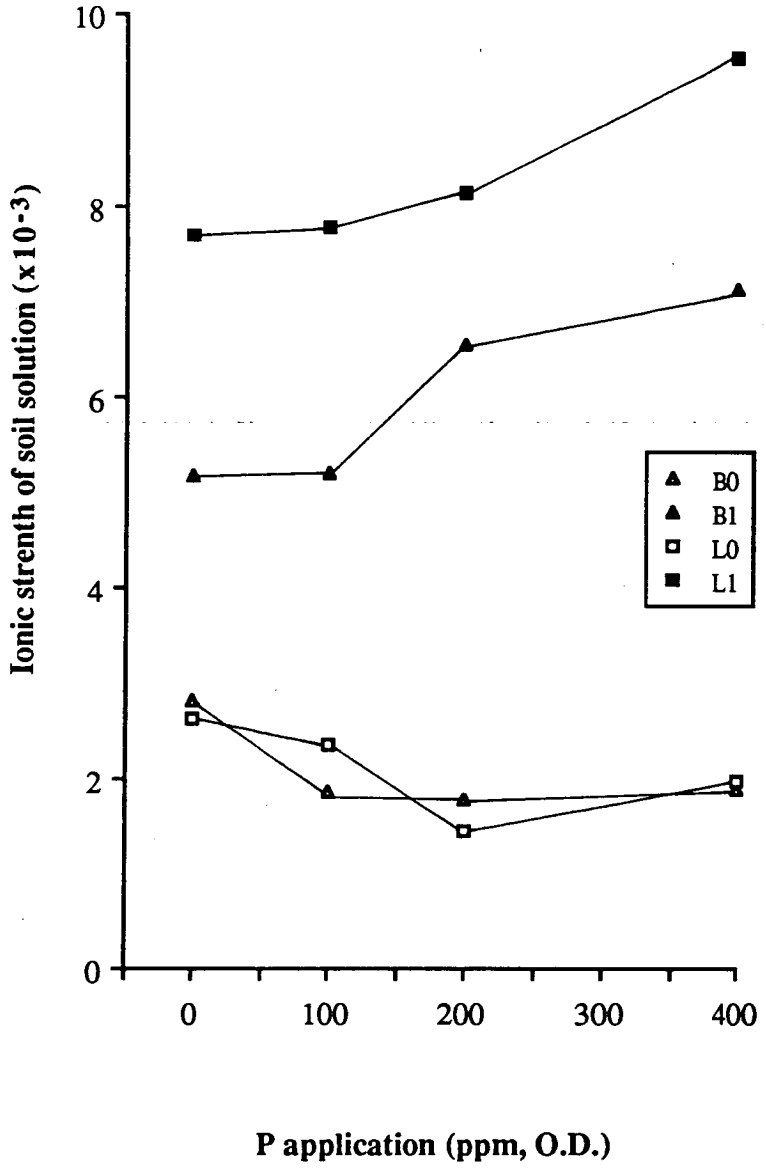


Figure 6.8 Effect of rate of phosphate application on soil solution ionic strength with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.7 Soil solution ionic strength ($x10^{-3}$) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	4.00	3.54	4.16	4.51	4.05
Lucerne chaff	5.17	5.06	4.79	5.75	5.19
mean (P)	4.58	4.3	4.47	5.13	

LSD (0.05); O.M. type (T) = 0.38** T x P = NS
P application (P) = NS

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	2.73	2.11	1.6	1.93	2.09
With O.M.	6.44	6.48	7.35	8.33	7.15

LSD (0.05); O.M. rate (R) = 1.17 *** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	2.09	6.02	4.05
Lucerne chaff	2.10	8.28	5.19

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	2.82	1.87	1.77	1.90	5.18	5.20	6.56	7.12
Lucerne chaff	2.64	2.35	1.44	1.97	7.70	7.77	8.14	9.54

LSD (0.05); T x R x P = NS

6.3.4. Soil and plant phosphorus

Available phosphorus: This increased ($P<0.001$) with rate of phosphorus application, was higher with than without added organic matter ($P<0.01$) and higher ($P<0.05$) following addition of lucerne chaff than after addition of barley straw (Figure 6.9, Table 6.8; Appendix 6.4). These results could be due to the direct effect of phosphorus application and are also in accord with those of Awad et al. (1976) which were attributed to reduced concentration of active aluminium and increased pH. Associated effects were enhanced phosphorus availability and increased plant uptake of phosphorus.

Plant uptake of phosphorus: Uptake increased sharply ($P<0.001$) with rate of phosphorus application as seen in concentration and content of plant tops (Figure 6.10, 6.11; Table 6.9, 6.10; Appendix 6.5). Uptake was further enhanced ($P<0.01$) by added organic matter. It has been shown that active soil aluminium was depressed by application of organic matter and soluble phosphate. These effects are now seen to be reflected in higher phosphorus concentrations and content of plant tops with increases of more than 80 percent over controls.

Thus fertilizer phosphate is benificial not only directly as a plant nutrient but also in alleviation of aluminium toxicity (Haynes, 1984). It has also been found that various decomposition products of organic matter including. simple organic acids, lignin and humus itself can form stable complexes or chelates with polyvalent cations associated with phosphorus fixation (Khanna and Stevensosn, 1962; Nagarajah et al., 1970). Furthermore it has been shown that various organic acids are able to release phosphorus in more soluble form from less soluble iron, aluminium and calcium phosphates (Johnston, 1959) with citric acid more effective than other organic acids, succinic, malic, oxalic , tartaric and lactic acids.

6.3.5. Plant response and dry matter production

Plant response was assessed on visual plant symptoms and dry matter production. However actual phosphorus deficiency symptoms were observed only in response to nil addition of phosphorus (P, 0 ppm) both with and without added

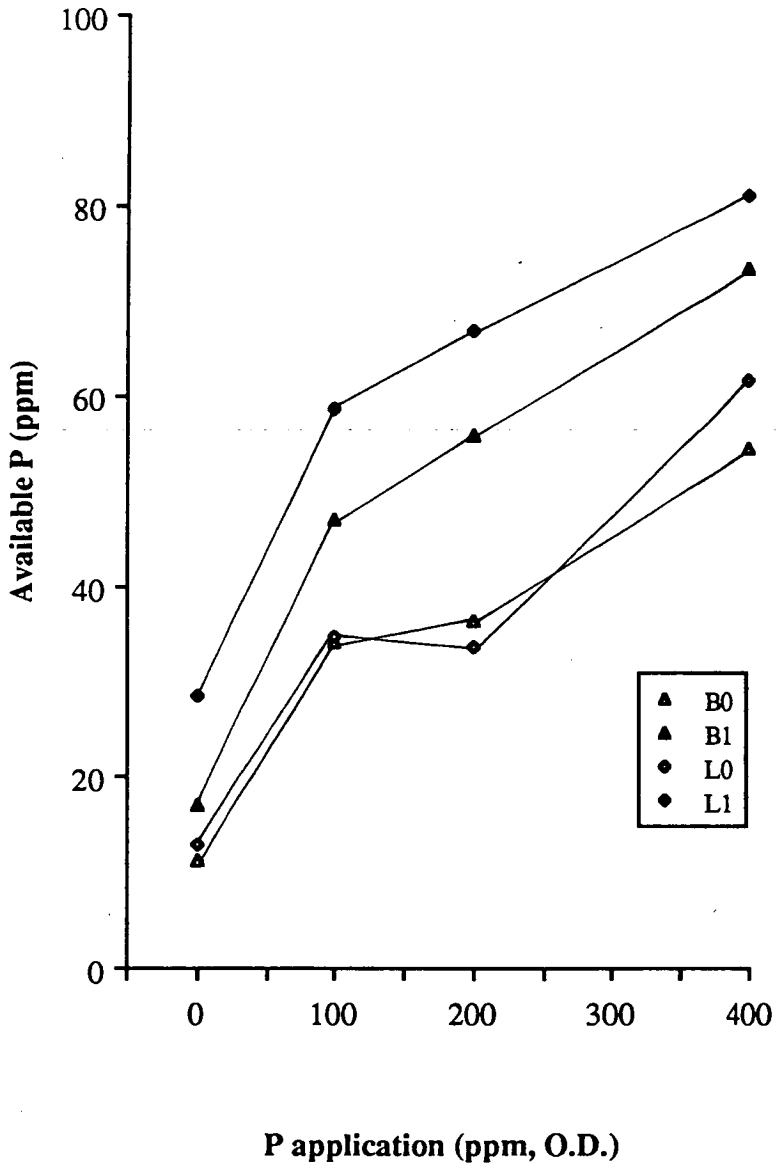


Figure 6.9 Effect of rate of phosphate application on available phosphorus with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.8 Available phosphorus (µg/g O.D.soil) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	14.21	40.58	46.19	63.96	41.23
Lucerne chaff	20.77	46.71	50.28	71.38	47.28
mean (P)	17.49	43.64	48.23	67.67	

LSD (0.05); O.M. type (T) = 5.55 * T x P = NS
P application (P) = 2.92 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	12.16	34.49	35.03	58.10	34.94
With O.M.	22.82	52.79	61.43	77.24	53.57

LSD (0.05); O.M. rate (R) = 9.57 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	34.10	48.37	41.23
Lucerne chaff	35.79	58.78	47.28

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	11.34	34.11	36.45	54.50	17.08	47.05	55.92	73.42
Lucerne chaff	12.98	34.87	3.62	61.71	28.57	58.54	66.95	81.06

LSD (0.05); T x R x P = NS

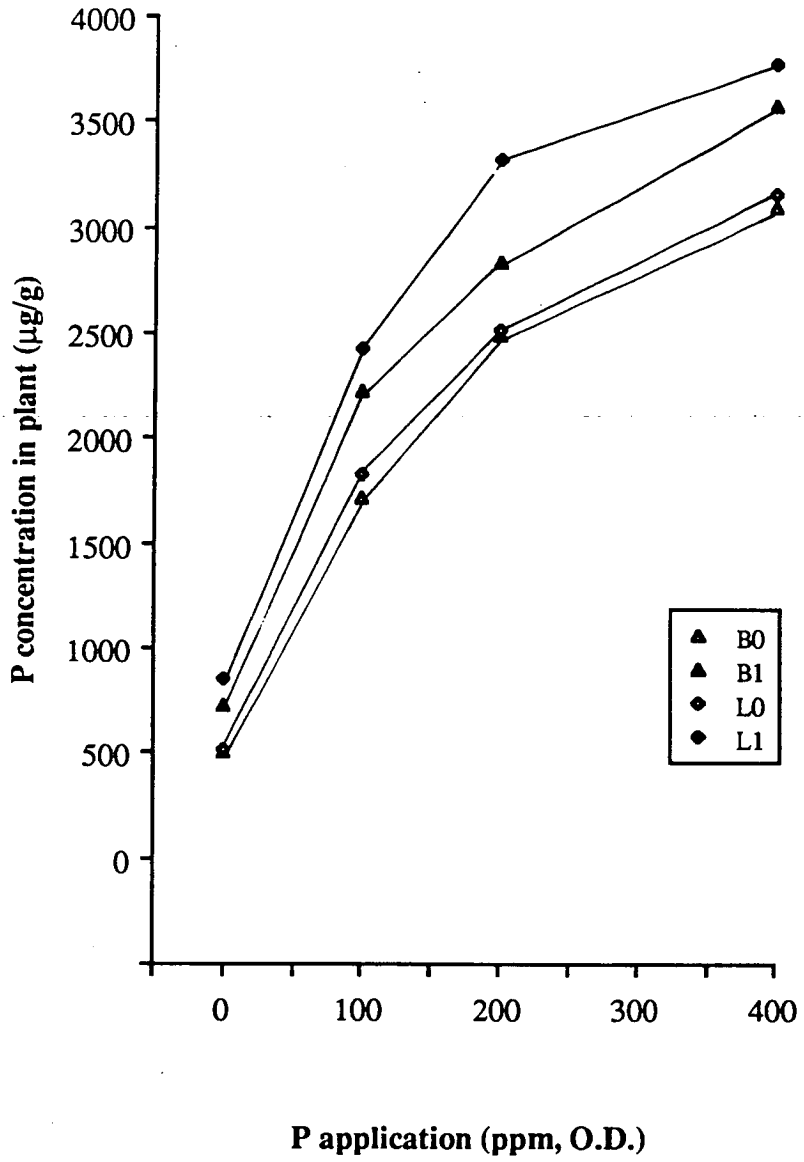


Figure 6.10 Effect of rate of phosphate application on phosphorus concentration of plant tops with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

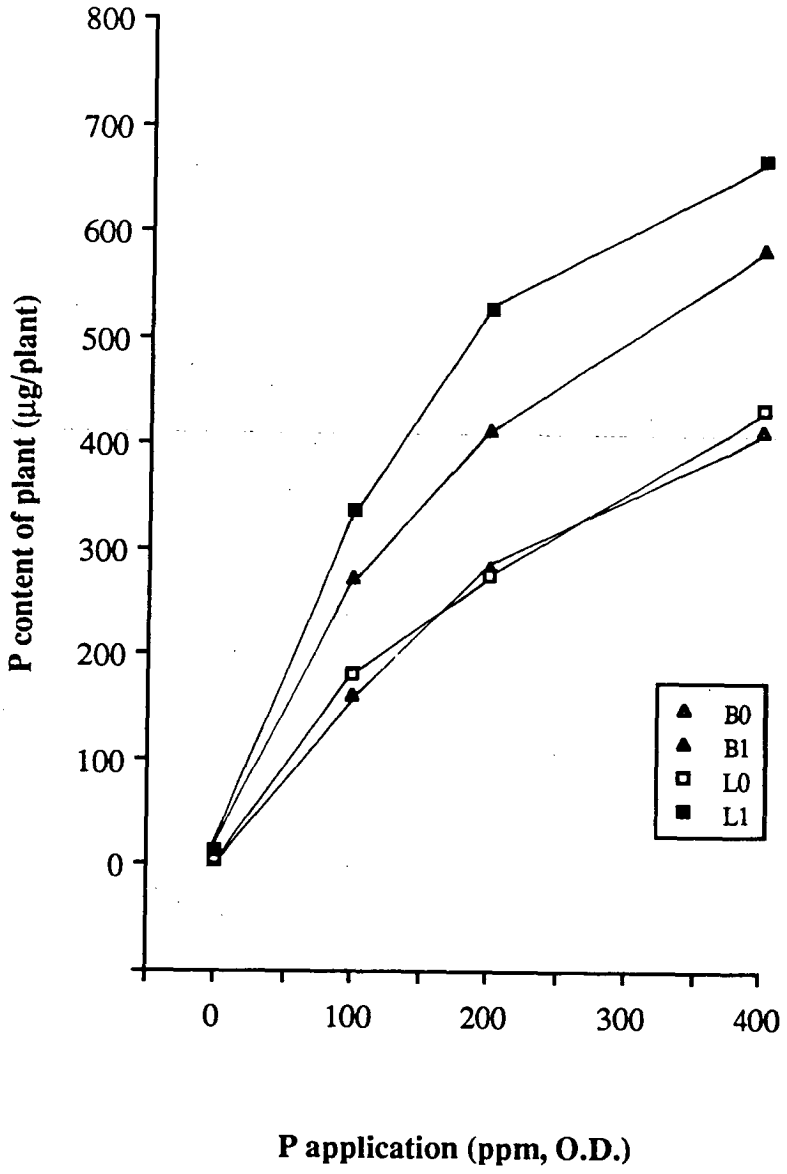


Figure 6.11 Effect of rate of phosphate application on phosphorus content of plant tops with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

Table 6.9 Phosphorus concentration of plant tops (μg/g) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	619.6	1972.3	2661.9	3335.7	2147.4
Lucerne chaff	681.0	2127.5	2917.8	3468.6	2298.7
mean (P)	650.3	2049.9	2789.9	3402.2	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 257.6 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	512.9	1772.1	2498.6	3126.8	1977.6
With O.M.	787.7	2327.7	3081.1	3677.6	2468.5

LSD (0.05); O.M. rate (R) = 259.0 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	1952.65	2342.15	2147.40
Lucerne chaff	2002.55	2594.93	2298.74

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	509.6	1718.8	2485.7	3096.5	729.6	2225.8	2838.2	3575.0
Lucerne chaff	516.2	1825.4	2511.5	3157.1	845.8	2429.6	3324.1	3780.2

LSD (0.05); T x R x P = NS

Table 6.10 Phosphorus content of plant tops (µg/plant) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	6.41	216.70	347.46	498.17	267.18
Lucerne chaff	9.61	257.73	400.04	550.35	304.43
mean (P)	8.01	237.21	373.75	524.26	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 60.05 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	4.89	170.61	278.77	423.29	219.39
With O.M.	11.11	303.81	468.72	625.22	352.22

LSD (0.05); O.M. rate (R) = 43.37 ** R x P = 89.64 *

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	215.52	318.85	267.18
Lucerne chaff	223.27	385.6	304.43

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	4.50	161.27	282.80	413.52	8.31	272.13	412.12	582.82
Lucerne chaff	5.29	179.96	274.75	433.07	13.92	335.50	525.33	667.63

LSD (0.05); T x R x P = NS

organic matter. The lowest rate of phosphate application (P, 100 ppm) was sufficient to prevent appearance of deficiency symptoms. Phosphorus deficiency in plant tops was seen as a general reduction in growth together with dark green narrow leaves, purple stems and leaves, and browning of older leaf tips. Roots of phosphorus-deficient plants were stubby and brown and lacked fine branches.

Dry weight of both plant tops and roots increased ($P<0.001$) with rate of phosphate application (Figure 6.12, 6.13; Table 6.11, 6.12; Appendix 6.6). To further emphasize treatment effects relative yields of plant tops and roots were again calculated by assigning a value of 100 to the highest yield of tops and roots (P, 400 ppm; L1) with other yields calculated as percentages. At the lowest rate (P, 100 ppm), the increment of relative yield of both plant tops and roots was more than 40 percent above the control yield (P, 0 ppm; Bo, Lo) (Figure 6.14, 6.15). Yields increased further but less rapidly at higher rates of phosphate application.

Addition of organic matter further enhanced ($P<0.01$) yield of both plant tops and roots at all rates of phosphorus application with the highest yields in response to lucerne chaff at each level of phosphorus application.

The results show that phosphorus content of plant tops had a positive relation to soil available phosphorus ($r^2=0.94$) (Figure 6.16). The relative yield of plant tops and roots was also directly related ($r^2=0.92$, 0.90) to available phosphorus. The critical level (90% relative yield) under the conditions of this experiment was approximately 65 ppm (O.D.) available phosphorus (Figure 6.17).

Aluminium toxicity effects have been attributed to monomeric aluminium only (Blamey et al., 1983) the mechanism being the withholding of phosphorus from the plant due to its precipitation in very insoluble compounds with monomeric aluminium. The results of the present study strongly support this in that the main effect of added organic matter was a large reduction in monomeric aluminium in the soil solution with enhancement of phosphorus availability and plant uptake of phosphorus.

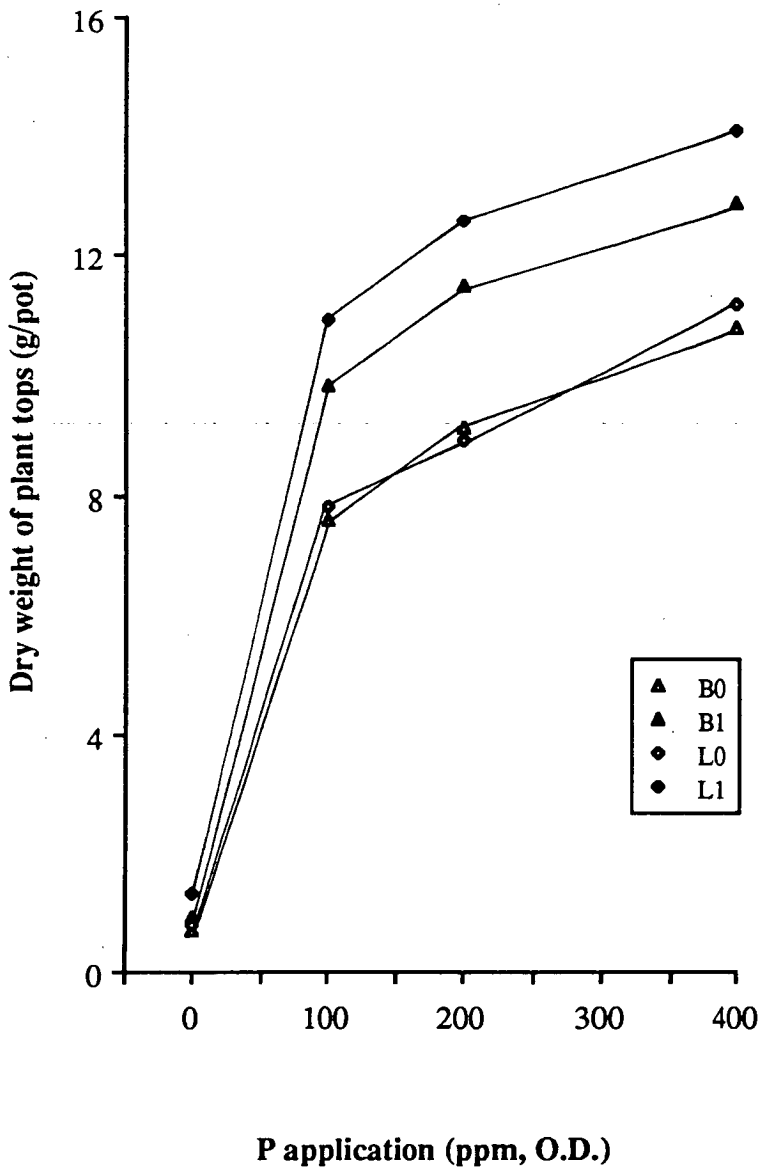


Figure 6.12 Effect of rate of phosphate application on dry weight of plant tops with and without organic matter added as barley straw (B1,Bo) or lucerne chaff (L1, Lo).

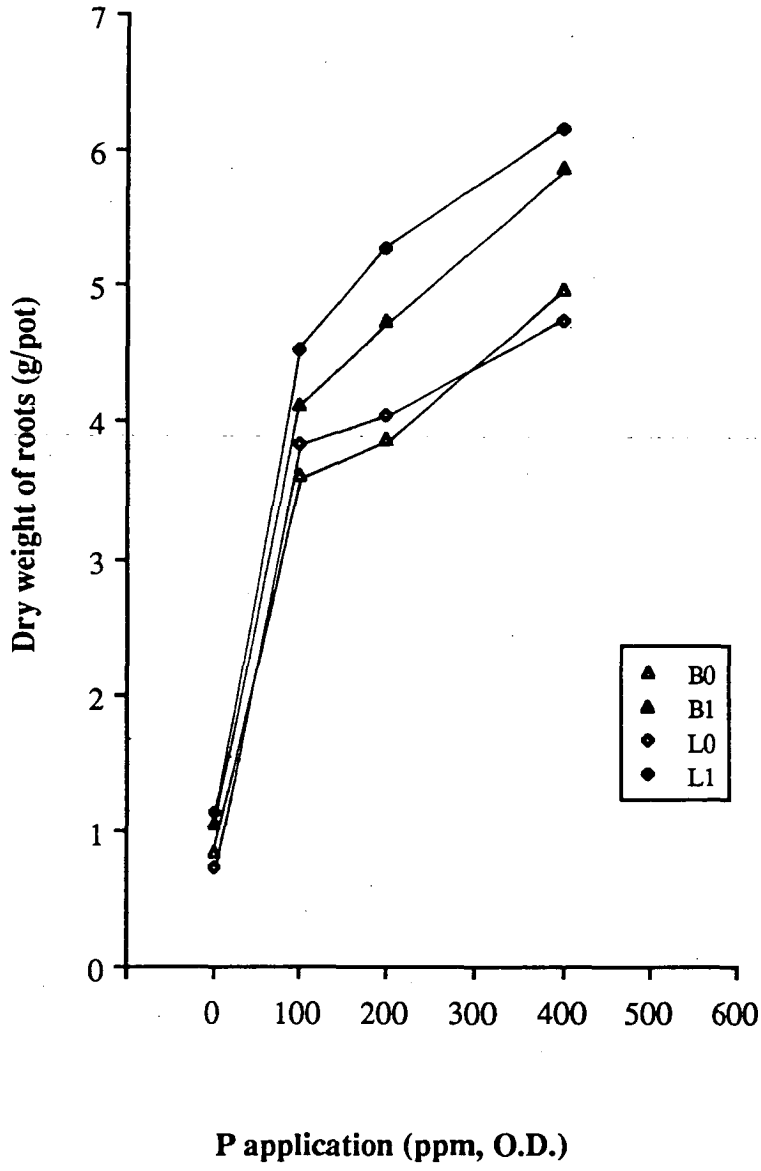


Figure 6.13 Effect of rate of phosphate application on dry weight of roots with and without organic matter added as barley straw (B1, Bo) or lucerne chaff.(L1, Lo).

Table 6.11 Dry weight of plant tops ($x10^{-1}$ g/pot) in relation to type and rate of organic matter and phosphorus application

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	0.80	8.68	10.30	11.85	7.91
Lucerne chaff	1.05	9.35	10.75	12.65	8,45
mean (P)	0.92	9.01	10.52	12.25	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 1.18 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	0.75	7.68	9.00	11.00	7.11
With O.M.	1.10	10.35	12.05	13.50	9.25

LSD (0.05); O.M. rate (R) = 0.7 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	7.04	8.78	7.91
Lucerne chaff	7.18	9.73	8.45

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	0.70	7.57	9.10	10.80	0.90	9.80	11.50	12.90
Lucerne chaff	0.80	7.80	8.90	11.20	1.30	10.90	12.60	14.10

LSD (0.05); T x R x P = NS

Note: Calculation of analysis of variance was based on multiplication transformed data (x 10)

Table 6.12 Dry weight of roots ($x10^{-1}$ g/pot) in relation to type and rate of organic matter and phosphorus application (Means of three replicates)

i. Organic matter type (T) x P application (P)

(P)	0	100	200	400	mean
O.M. type					
Barley straw	0.95	3.87	4.30	5.41	3.63
Lucerne chaff	0.93	4.18	4.66	5.44	3.80
mean (P)	0.94	4.02	4.48	5.42	

LSD (0.05); O.M. type (T) = NS T x P = NS
P application (P) = 0.23 ***

ii. Organic matter rate (R) x P applied (P)

(P)	0	100	200	400	mean
O.M. rate					
Without O.M.	0.79	3.72	3.95	4.84	3.32
With O.M.	1.09	4.32	5.01	6.00	4.11

LSD (0.05); O.M. rate (R) = 0.28 ** R x P = NS

iii. Organic matter type (T) x Organic matter rate (R)

O.M.rate (R)	without O.M.	with O.M.	mean
O.M.type (T)			
Barley straw	3.32	3.94	3.63
Lucerne chaff	3.33	4.27	3.80

LSD (0.05); T x R = NS

iv. Organic matter type x Organic matter rate x P application

O.M. rate	Without O.M.				With O.M.			
P application	0	100	200	400	0	100	200	400
O.M. type								
Barley straw	0.85	3.61	3.87	4.96	1.05	4.12	4.73	5.86
Lucerne chaff	0.73	3.83	4.04	4.73	1.13	4.53	5.28	6.15

LSD (0.05); T x R x P = NS

Note: Calculation of analysis of variance was based on multiplication transformed data (x 10)

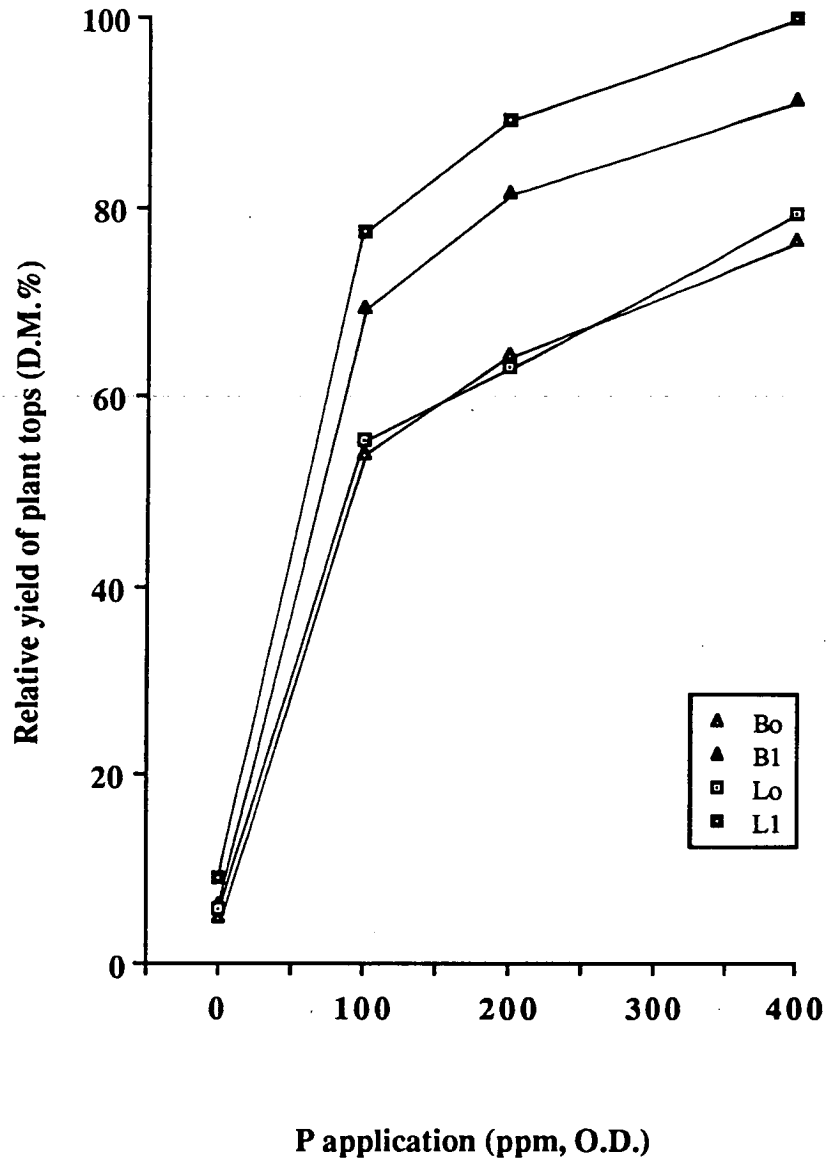


Figure 6.14 Effect of rate of phosphate application on relative yield of plant tops with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

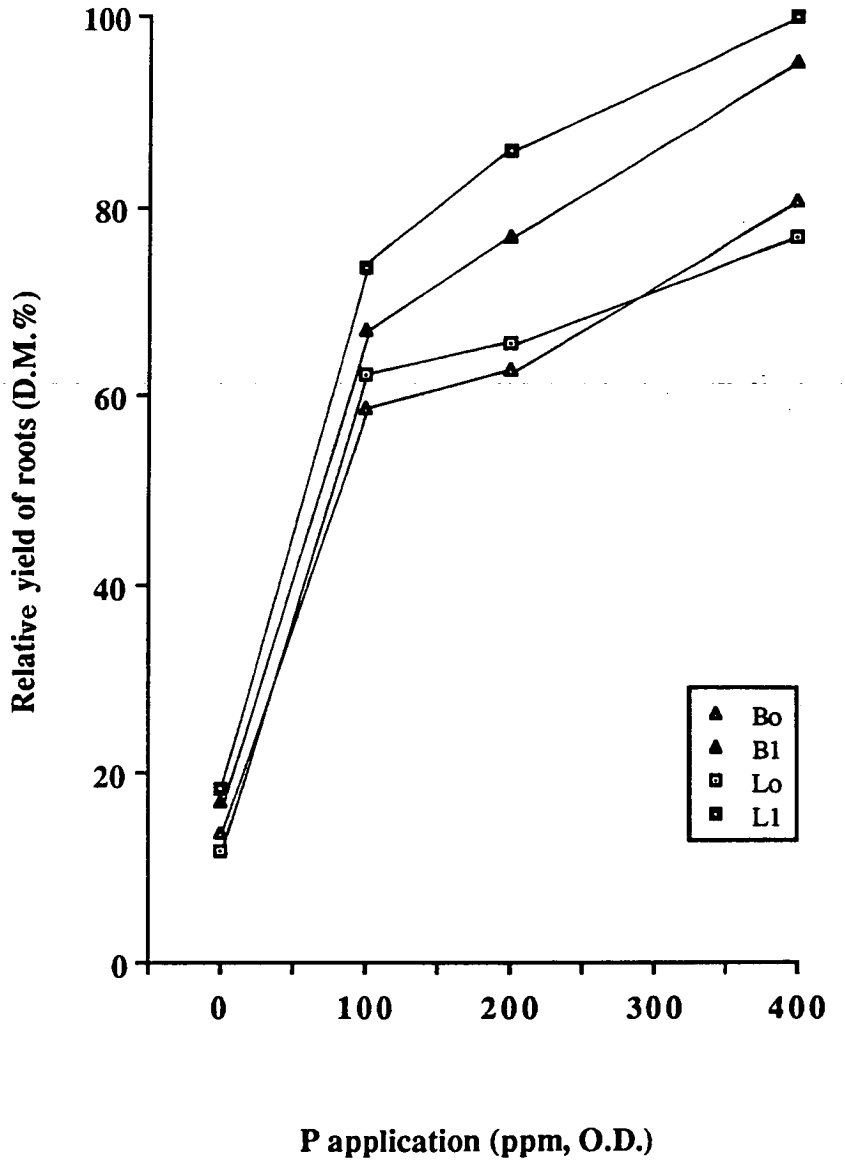


Figure 6.15 Effect of rate of phosphate application on relative yield of roots with and without organic matter added as barley straw (B1, Bo) or lucerne chaff (L1, Lo).

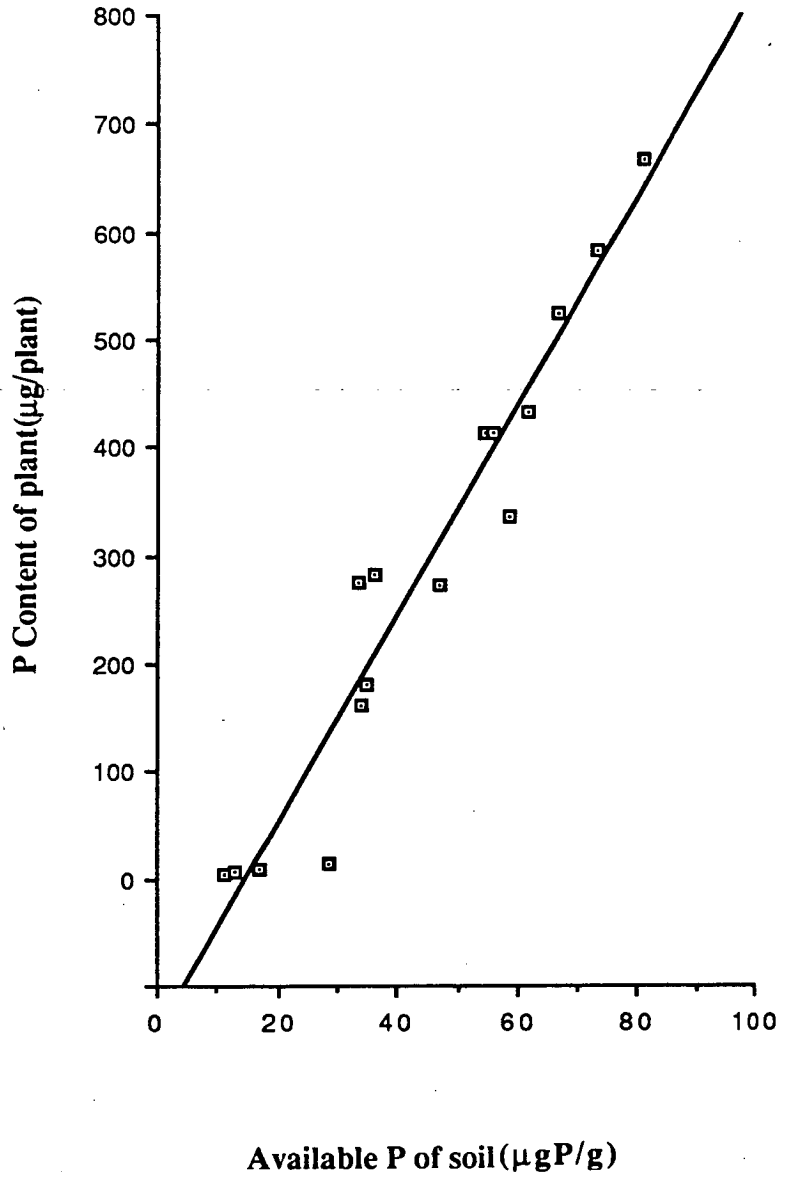


Figure 6.16 Relationship between available phosphorus and phosphorus content of plant, $Y = -140.8789+9.6403X$, $r^2 = 0.94$

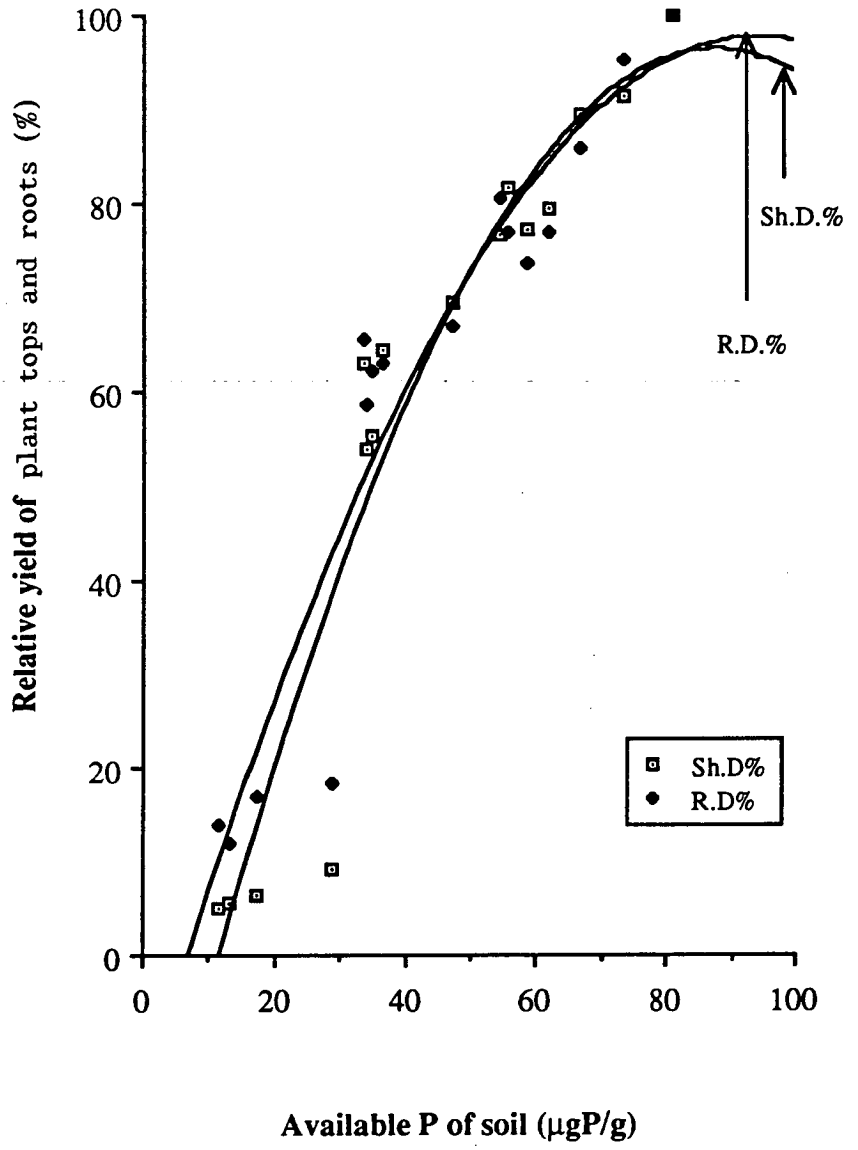


Figure 6.17 Curvinear relationship between available P and relative DM yield of plant tops and roots:

(ShD%); $Y = -31.3079+2.9155x-0.0166x^2$, $r^2=0.92$; and

(RD%); $Y = -15.6506+2.4087x-0.0128X^2$, $r^2 = 0.90$

7 GENERAL DISCUSSION AND CONCLUSIONS

Although the krasnozem soils used in the experiments reported here have a long history of arable use and application of fertilizer phosphorus as ordinary superphosphate, they are also known to have high phosphorus sorption capacities. This, and their strongly acid reaction (pH), has raised concern regarding both availability of phosphorus and active aluminium as growth-limiting factors.

The soil materials used were collected from the surface to a depth of 15 cm from typical areas of the Burnie, Lapoinya, and Yolla series which occur as a toposequence from low (near coast) to high (plateau top) elevation, with rainfall increasing in parallel. The Yolla soil had a higher pH than that shared by the Burnie and Lapoinya soils, a substantially higher ΣBEC and CEC and a much higher organic matter content, almost double that of the Burnie and Lapoinya soils which were similar in this property. Available P was much lower in the Burnie soil than in the Lapoinya and Yolla soils, paralleling P sorption capacity. Available Al showed an irregular pattern, being lowest in the Lapoinya soil, higher in the Yolla, and highest in the Burnie soil. Organic matter added to these soils resulted in measurable changes in the value of all properties studied (some of which were statistically significant) without causing significant change in their relativity as measured for the untreated soils.

Two forms of organic matter were used (barley straw and lucerne chaff) in the belief that effects of added organic matter on soils could be related to C/N ratio, which has been shown in many experiments to be a major factor in the effects of their decomposition on soil properties. Although there were, in the initial experiments, significant effects at both low and high rates of addition on I.S., available P and exchangeable Al, the effects were much greater at the higher rate and at this rate significant effects on ΣBEC and CEC were also measured. An increasing trend was observed in respect to pH, which was also higher in the lucerne chaff treated soils, but these differences were not statistically significant.

The greater effects of lucerne chaff in increasing ΣBEC and I.S. could be due to release of more organic anions than from barley straw over the period of the experiment, so decreasing the point of zero charge (Gillman, 1985) but not enough to cause a significant increase in CEC.

As described in Chapter 4, the rate of addition of organic matter in the second experiment was increased greatly (some 8 and 16 times respectively for low and high rates). This was done in consideration of the small magnitude of effects measured in the first experiment. The actual rates used were calculated to provide two and four times the initial level of Walkley-Black organic carbon in the Burnie clay loam topsoil used in this experiment. In the event there were no significant differences in the effects of these two levels of application.

Added urea had a confounding effect on soil reaction (pH), particularly notable in the early weeks of the experiment. The sharply increased pHs measured four weeks after establishment were probably due to hydrolysis of the added urea, formation of ammonia, and nitrogen immobilization (Hendrickson et al., 1987). However, the effect of urea on soil reaction declined gradually and the 16-week values were approaching those of the organic-matter-alone treatments.

Both the effect of urea in increasing pH and that of added organic matter contributed to reduced levels of exchangeable Al. For example, the rate of decrease of exchangeable Al was very rapid in the first four weeks as pH rose from 4.7 to 7.7, with a lower rate of decrease from weeks 4 to 8 followed by a return between weeks 8 and 16 to the absolute levels measured at week 4.

Even though there was a confounding effect of urea in the urea treatments addition of organic matter alone was followed by reduced levels of exchangeable Al as well as increased levels of available P. There was a good negative correlation between exchangeable Al and Available P with increasing time. The rate of decrease in available P appeared to be greater than the rate of increase in exchangeable Al. This may be due to immobilization of available P by soil microorganisms.

In the third experiment (Chapter 5),. an attempt was made to induce Al toxicity in test plants by direct application of soluble Al (1) after four weeks incubation of soil and organic matter added at the lower of the two higher rates used in the previous experiment (i.e. 80 g/klg soil) and (2) at the same time as addition of organic matter. Under the former condition there were greater effects attributed to increasiong available P and reducing aluminium toxicity. Reduced levels were measured of both exchangeable and solution Al. Such effects may be due to the formation of aluminium-organic complexes, reducing the level of soil solution Al, presumably monomeric in character, and reaction with soluble P.

This would explain the positive effects on levels of available P and P uptake associated with increasing plant yields. The relative dry matter yields of plant tops and roots exceeded 90% of maximum yield when the concentration of soil solution P was greater than 0.15 μg P/ml for both barley straw and lucerne chaff treatments. The data also indicate that the relative dry matter yield of tops and roots of the test plant exceeded 90% under the conditions of this experiment provided that the level of soil solution Al was below 5 μM (Table 5.2).

Although substantial positive effects were measured after addition of organic matter and soluble Al together immediately before sowing of seed of the test plant, the effects were greater when soil plus organic matter was incubated for one month prior to addition of soluble Al and subsequent sowing. Although probably no more than a time effect, there is a practical management implication for early addition of decomposable organic matter in relation to sowing time.

Finally, there were different effects on this Burnie clay loam soil in relation to whether or not a period of incubation was allowed in relation to levels of soluble (monomeric) Al, exchangeable Al and P sorption. There were no differences that were statistically significant in soil reaction (pH), available P, P uptake, or shoot and root dry weights.

In the final experiment (Chapter 6),.the Lapoinya soil was used as substrate to test the effects of added organic matter and added soluble P on soil

aluminium and the growth of a test plant. The chief results of this experiment were that added organic matter was effective not only in detoxificiation of monomeric Al and in reducing exchangeable and soluble (monomeric) Al, but also in enhancing the efficiency of the applied fertiliser P. Possible reasons for these effects are suppression of soil acidity by a buffering effect of added, decomposable organic matter and complexing of Al ions in organic forms that are non-toxic to the plant and non reactive, or less reaction, with soluble P. There was a strong positive correlation between P uptake and available P and the curvilinear relationship suggested a 90% relative yield for both tops and roots at about 65 μg P/g soil of available P.

Traditional amelioration of acid soils is by liming and this technique has been used on soils of which those used in the present study are representative in Tasmania. The results now reported indicate that management of soil organic matter may offer at least a partial alternative to regular liming. It should certainly be of value in reducing the frequency of liming and the amounts of lime required. Conservation or addition of organic matter should also be beneficial in amelioration of other very important soil physical qualities.

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APPENDIX 3.1

ANALYSIS OF VARIANCE OF CATION EXCHANGE CAPACITY AND BASIC EXCHANGEABLE CATTONS (meq/100 g)

Source of Variation	D.F.	CEC		BEC	
		M.S.	V.R.	M.S.	V.R.
Block	2	2.570	1.414^{ns}	0.048	0.068^{ns}
Soil (S)	2	64.033	35.231^{**}	74.485	105.354^{***}
Error	4	1.817		0.707	
Organic matter (O)	1	3.435	5.007^{ns}	6.791	6.860^{*}
S x O	2	0.035	0.051^{ns}	0.725	0.732^{ns}
Error	6	0.686		0.990	
Rate (R)	2	2.429	0.707^{ns}	1.109	0.703^{ns}
S x R	4	0.065	0.019^{ns}	0.032	0.020^{ns}
Error	12	3.436		1.577	
O x R	2	0.400	0.178^{ns}	0.430	0.104^{ns}
S x O x R	4	0.014	0.006^{ns}	0.226	0.055^{ns}
Error	12	2.245		4.138	

APPENDIX 3.2

ANALYSIS OF VARIANCE OF SOIL pH AND IONIC STRENGTH OF SOIL SOLUTION

Source of Variation	D.F.	pH		Ionic Strength	
		M.S.	V.R.	M.S.	V.R.
Block	2	0.040	0.176^{ns}	0.487	1.777^{ns}
Soil (S)	2	0.043	0.192^{ns}	6.302	23.00^{**}
Error	4	0.225		0.274	
Organic matter (O)	1	0.013	0.082^{ns}	13.168	10.568^{*}
S x O	2	0.006	0.038^{ns}	0.503	0.404^{ns}
Error	6	0.159		1.246	
Rate (R)	2	0.048	0.168^{ns}	8.118	15.146^{***}
S x R	4	0.002	0.007^{ns}	0.036	0.067^{ns}
Error	12	0.286		0.536	
O x R	2	0.001	0.002^{ns}	2.570	2.567^{ns}
S x O x R	4	0.001	0.002^{ns}	0.183	0.183^{ns}
Error	12	0.406		1.001	

APPENDIX 3.3

ANALYSIS OF VARIANCE OF EXTRACTABLE PHOSPHORUS AND ALUMINIUM CONCENTRATION IN SOIL(µg/gram)

Source of Variation	D.F.	P (µg/gram)		Al (µg/gram)	
		M.S.	V.R.	M.S.	V.R.
Block	2	18.203	0.477^{ns}	1.887	0.178^{ns}
Soil (S)	2	2025.759	53.048^{***}	1557.973	146.95^{***}
Error	4	38.187		10.602	
Organic matter (O)	1	100.396	2.350^{ns}	51.666	3.256^{ns}
S x O	2	10.094	0.236^{ns}	5.425	0.342^{ns}
Error	6	42.714		15.868	
Rate (R)	2	233.357	7.289^{**}	263.548	16.489^{***}
S x R	4	3.990	0.125^{ns}	3.986	0.249^{ns}
Error	12	32.017		15.983	
O x R	2	16.186	0.154^{ns}	28.787	0.909^{ns}
S x O x R	4	14.388	0.137^{ns}	7.739	0.244^{ns}
Error	12	105.116		31.674	

APPENDIX 4.1

ANALYSIS OF VARIANCE OF SOIL pH AT
DIFFERENT PERIODS OF INCUBATION

Source of Variation	D.F.	Soil pH at 0 week		Soil pH after 4 weeks		Soil pH after 8 weeks		Soil pH after 16 weeks	
		M.S.	V.R.	M.S.	V.R.	M.S.	V.R.	M.S.	V.R.
Block	2	0.304	0.976^{ns}	0.381	3.197^{ns}	0.142	2.185^{ns}	0.112	0.862^{ns}
Type O.M. (T)	1	0.178	0.573^{ns}	2.544	21.378^{*}	1.588	24.431^{*}	0.640	4.944^{ns}
Error	2	0.311		0.119		0.065		0.130	
Urea-N (N)	1	19.345	51.177^{**}	9.641	8.240^{*}	9.000	32.727^{**}	2.310	9.747^{*}
T x N	1	0.178	0.471^{ns}	0.189	0.162^{ns}	0.040	0.145^{ns}	0.068	0.287^{ns}
Error	4	0.378		1.170		0.275		0.237	
Rate O.M. (R)	2	5.956	39.184^{***}	10.196	52.829^{***}	10.159	43.978^{***}	6.162	15.103^{**}
T x R	2	0.036	0.237^{ns}	0.780	4.041^{ns}	0.511	2.212^{ns}	0.204	0.500^{ns}
Error	8	0.152		0.193		0.231		0.408	
N x R	2	5.312	9.402^{**}	2.680	13.137^{**}	2.687	4.617^{*}	0.610	0.757^{ns}
T x N x R	2	0.051	0.090^{ns}	0.042	0.206^{ns}	0.093	0.160^{ns}	0.036	0.045^{ns}
Error	8	0.565		0.204		0.582		0.806	

APPENDIX 4.2

ANALYSIS OF VARIANCE OF SOIL ALUMINIUM AT DIFFERENT PERIODS OF INCUBATION

Source of Variation	D.F.	Soil Al at 0 week		Soil Al after 4 weeks		Soil Al after 8 weeks		Soil Al after 16 weeks	
		M.S.	V.R.	M.S.	V.R.	M.S.	V.R.	M.S.	V.R.
Block	2	7.427	2.049^{ns}	0.526	0.097^{ns}	5.790	0.221^{ns}	5.083	0.541^{ns}
Type of O.M. (T)	1	113.956	31.436^{*}	101.204	18.573^{**}	85.964	3.28^{ns}	48.164	5.127^{ns}
Error	2	3.625		5.449		26.205		9.395	
Urea-N (N)	1	1532.331	108.985^{**}	153.017	4.352^{*}	943.821	19.166^{*}	88.297	84.495^{**}
T x N	1	1.177	0.084^{ns}	51.265	1.458^{ns}	9.662	0.196^{ns}	2.454	2.348^{ns}
Error	4	14.060		35.163		49.244		1.045	
Rate of O.M. (R)	2	2116.649	90.660^{***}	9196.158	534.350^{***}	2917.921	112.318^{***}	8637.037	159.916^{***}
T x R	2	3.796	0.163^{ns}	47.049	2.734^{ns}	78.578	3.025^{ns}	16.242	0.301^{ns}
Error	8	23.347		17.210		25.979		54.010	
N x R	2	359.182	25.467^{**}	19.658	0.347^{ns}	296.272	4.421^{*}	9.400	0.108^{ns}
T x N x R	2	16.061	1.139^{ns}	11.157	0.197^{ns}	2.658	0.040^{ns}	3.514	0.040^{ns}
Error	8	14.104		56.573		67.016		86.789	

APPENDIX 4.3

ANALYSIS OF VARIANCE OF SOIL PHOSPHORUS AT DIFFERENT PERIODS OF INCUBATION

Source of Variation	D.F.	Soil P at 0 week		Soil P after 4 weeks		Soil P after 8 weeks		Soil P after 16 weeks	
		M.S.	V.R.	M.S.	V.R.	M.S.	V.R.	M.S.	V.R.
Block	2	49.152	2.481^{ns}	28.50	5.06^{ns}	45.422	0.718^{ns}	65.096	6.753^{ns}
Type O.M.(T)	1	50.410	2.544^{ns}	137.945	24.476^{*}	83.174	1.315^{ns}	93.187	9.667^{ns}
Error	2	19.813		5.636		63.266		9.640	
Urea-N (N)	1	247.433	3.755^{ns}	175.695	8.289^{*}	412.903	4.182^{ns}	165.294	30.913^{**}
T x N	1	4.753	0.072^{ns}	0.018	0.001^{ns}	4.537	0.046^{ns}	141.293	26.425^{**}
Error	4	65.889		21.195		98.743		5.347	
Rate O.M. (R)	2	1028.362	29.946^{***}	4010.493	40.027^{***}	2112.749	13.583^{**}	500.645	13.180^{**}
T x R	2	20.765	0.605^{ns}	25.777	0.257^{ns}	18.927	0.122^{ns}	11.578	0.305^{ns}
Error	8	34.340		100.195		155.543		37.984	
N x R	2	68.273	0.544^{ns}	61.900	1.234^{ns}	81.920	0.664^{ns}	28.836	0.488^{ns}
T x N x R	2	5.095	0.041^{ns}	14.337	0.286^{ns}	6.852	0.056^{ns}	4.567	0.077^{ns}
Error	8	125.569		50.166		123.371		59.122	

APPENDIX 4.4

ANALYSIS OF VARIANCE OF SOIL SOLUTION IONIC STRENGTH (I.S.)
AT DIFFERENT PERIODS OF INCUBATION

Source of Variation	D.F.	I.S. at 0 week		I.S. after 4 weeks		I.S. after 8 weeks		I.S. after 16 weeks	
		M.S.	V.R.	M.S.	V.R.	M.S.	V.R.	M.S.	V.R.
Block	2	0.109	3.516^{NS}	1.954	1.055^{NS}	0.534	4.413^{NS}	0.32	0.87^{NS}
Type O.M. (T)	1	0.596	19.226^{*}	47.156	25.462^{*}	30.404	251.24^{***}	33.26	89.89^{**}
Error	2	0.031		1.852		0.121		0.37	
Urea-N (N)	1	1.319	5.496^{NS}	14.746	8.045^{*}	36.104	55.205^{**}	18.25	60.837^{**}
T x N	1	0.192	0.80^{NS}	2.843	1.551^{NS}	7.816	11.951^{*}	2.465	8.217^{*}
Error	4	0.240		1.833		0.654		0.30	
Rate O.M. (R)	2	5.890	64.022^{***}	365.74	244.317^{***}	380.91	275.82^{***}	315.75	362.93^{***}
T x R	2	0.317	3.446^{NS}	14.51	9.693^{**}	11.85	8.58^{*}	7.93	9.11^{**}
Error	8	0.092		1.497		1.381		0.87	
N x R	2	0.320	1.013^{NS}	3.348	0.449^{NS}	6.176	2.93^{NS}	3.364	0.92^{NS}
T x N x R	2	0.494	1.563^{NS}	2.659	0.357^{NS}	1.687	0.80^{NS}	0.908	0.25^{NS}
Error	8	0.316		7.456		2.109		3.66	

Appendix 4.5 pH and ionic strength of soil at different time of incubation

Treatments			pH				Ionic strength			
TOM	N	ROM	Time 1	Tiime 2	Time 3	Time 4	Time 1	Time 2	Time 3	Time 4
B	No	Ro	4.62	4.87	4.88	4.82	3.54	5.1	3.49	4.17
		R1	4.70	5.02	5.24	5.34	4.32	10.1	9.29	9.74
		R2	4.75	5.24	5.29	5.40	4.6	12.67	10.16	11.55
	N1	Ro	4.65	4.87	4.82	4.83	3.84	5.24	3.98	4.81
		R1	6.18	6.50	6.49	6.00	4.4	13.91	13.83	13.44
		R2	7.22	7.30	7.30	6.50	4.92	14.26	13.93	13.06
L	No	Ro	4.67	4.85	4.85	4.80	3.73	4.99	3.28	4.46
		R1	4.71	6.18	5.94	5.72	4.19	14.62	13.26	13.42
		R2	4.69	6.13	6.08	6.10	4.87	16.82	14.71	14.92
	N1	Ro	4.69	4.83	4.78	4.81	3.43	5.07	3.48	4.68
		R1	6.69	7.27	7.33	6.29	5.26	15.12	14.54	14.80
		R2	7.51	7.73	7.56	6.78	5.67	18.39	16.44	16.02

TRIPLICATE MEAN

TOM (B, L) is type of organic matter (Barley straw and Lucerne chaff),

N (No, N1) is nitrogen addition (Without N and With N),
ROM (Ro, R1, R2) is rate of organic matter (0, 80, and 160 g/kg soil),

Time 1, 2, 3, and 4 are Times after 0, 4, 8 and 16 weeks of incubation

Appendix 4.6 Exchangeable Al and P concentrations (μg/g) of soil at different time of incubation

Treatments TOM	N	ROM	Exchangeable Al Time 1	Tiime 2	Time 3	Time 4	Available P Time 1	Time 2	Time 3	Time 4
B	No	Ro	112.09	79.04	55.47	78.28	79.77	72.97	71.22	66.60
		R1	99.73	39.26	33.83	38.93	84.54	99.25	83.12	71.36
		R2	95.76	36.94	32.99	34.03	90.92	101.32	91.93	75.40
	N1	Ro	108.74	82.11	56.74	78.95	77.55	75.61	74.14	64.85
		R1	81.14	36.00	17.08	34.83	92.38	100.42	93.49	71.44
		R2	77.47	31.92	20.86	29.63	98.85	110.90	101.09	78.04
L	No	Ro	106.68	84.26	54.79	80.33	77.18	75.66	73.19	65.52
		R1	97.96	37.54	43.54	35.96	88.23	102.80	86.75	69.08
		R2	91.18	30.54	36.34	29.58	94.74	106.96	97.58	76.52
	N1	Ro	109.12	78.84	55.65	77.48	78.97	73.99	72.46	68.99
		R1	76.09	29.24	25.10	31.73	97.62	108.39	99.14	79.21
		R2	72.55	24.73	20.09	25.69	101.47	116.16	104.11	87.67

TRIPLICATE MEAN

TOM (B, L) is type of organic matter (Barley straw and Lucerne chaff),
N (No, N1) is nitrogen addition (Without N and With N),
ROM (Ro, R1, R2) is rate of organic matter (0, 80, and 160 g/kg soil),
Time 1, 2, 3, and 4 are Times after 0, 4, 8 and 16 weeks of incubation

APPENDIX 5.1

ANALYSIS OF VARIANCE OF EXCHANGEABLE ALUMINIUM AND MONOMERIC ALUMINIUM CONCENTRATION IN SOIL AND SOIL SOLUTION

Source of Variation	D.F.	AL (µg/gram)		Monomeric Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	101.316	1.94^{ns}	39.581	1.840^{ns}
Type O.M. (T)	1	993.174	19.015^{*}	10.547	0.490^{ns}
Error	2	52.23		21.507	
Rate O.M. (R)	1	130568.999	1339.980^{***}	2395.035	191.587^{***}
T x R	1	1073.711	11.019^{*}	8.069	0.645^{ns}
Error	4	97.441		12.501	
Rate Al (A)	3	3524.085	17.236^{***}	1248.158	64.604^{***}
T x A	3	56.224	0.275^{ns}	5.100	0.264^{ns}
Error	12	204.466		19.320	
R x A	3	1749.462	4.982^{*}	439.883	10.999^{**}
T x R x A	3	57.781	0.165^{ns}	18.051	0.451^{ns}
Error	12	351.188		39.994	

APPENDIX 5.2

ANALYSIS OF VARIANCE OF TOTAL AND ORGANIC ALUMINIUM CONCENTRATION IN SOIL SOLUTION

Source of Variation	D.F.	Total Al (µM)		Organic Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	38.819	7.764^{ns}	5.307	0.876^{ns}
Type O.M. (T)	1	654.016	130.803^{**}	498.456	82.253^{**}
Error	2	5.0		6.06	
Rate O.M. (R)	1	2.067	0.336^{ns}	2256.392	235.458^{***}
T x R	1	419.492	68.177^{**}	311.203	32.474^{**}
Error	4	6.153		9.583	
Rate Al (A)	3	2075.622	219.992^{***}	107.659	10.501^{**}
T x A	3	32.328	3.426^{ns}	19.681	1.920^{ns}
Error	12	9.435		10.252	
R x A	3	100.417	1.665^{ns}	145.010	7.964^{**}
T x R x A	3	32.271	0.535^{ns}	9.183	0.504^{ns}
Error	12	60.297		18.208	

APPENDIX 5.3

ANALYSIS OF VARIANCE OF SOIL pH AND IONIC STRENGTH IN SOIL SOLUTION

Source of Variation	D.F.	pH		Ionic Strength	
		M.S.	V.R.	M.S.	V.R.
Block	2	0.055	1.582^{ns}	0.027	0.141^{ns}
Type O.M. (T)	1	0.066	1.886^{ns}	0.02	0.104^{ns}
Error	2	0.035		0.192	
Rate O.M. (R)	1	8.467	46.779^{**}	1293.95	7748.204^{***}
T x R	1	0.105	0.580^{ns}	1.271	7.611^{ns}
Error	4	0.181		0.167	
Rate Al (A)	3	0.339	5.136^{*}	6.344	17.054^{***}
T x A	3	0.003	0.045^{ns}	0.083	0.223^{ns}
Error	12	0.066		0.372	
R x A	3	0.004	0.087^{ns}	0.239	0.705^{ns}
T x R x A	3	0.004	0.087^{ns}	0.197	0.581^{ns}
Error	12	0.046		0.339	

APPENDIX 5.4

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION

IN SOIL AND SOIL SOLUTION

Source of Variation	D.F.	P in soil (µg/gram)		P in soil solution (µg/gram)	
		M.S.	V.R.	M.S.	V.R.
Block	2	209.552	12.628^{ns}	0.017	2.830^{ns}
Type O.M. (T)	1	996.087	60.027^{*}	0.120	20.0^{*}
Error	2	16.594		0.006	
Rate O.M. (R)	1	4581.348	16.729^{*}	4.083	272.200^{***}
T x R	1	370.408	1.353^{ns}	0.141	9.400^{*}
Error	4	273.851		0.015	
Rate Al (A)	3	2520.294	7.875^{**}	2.142	23.800^{***}
T x A	3	17.384	0.054^{ns}	0.007	0.078^{ns}
Error	12	320.031		0.090	
R x A	3	99.305	0.199^{ns}	0.124	0.992^{ns}
T x R x A	3	9.161	0.018^{ns}	0.009	0.072^{ns}
Error	12	499.811		0.125	

APPENDIX 5.5

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION

AND CONTENT IN PLANT

Source of Variation	D.F.	P Concentration (µg/g)		P Content (µg/plant)	
		M.S.	V.R.	M.S.	V.R.
Block	2	16442.188	0.982^{ns}	2204.46	1.779^{ns}
Type O.M. (T)	1	57028.453	3.406^{ns}	6685.881	5.397^{ns}
Error	2	16744.0		1238.75	
Rate O.M. (R)	1	858755.110	60.215^{**}	181314.372	360.102^{***}
T x R	1	39519.984	2.771^{ns}	8036.780	15.962^{*}
Error	4	14261.570		503.508	
Rate Al (A)	3	729089.657	19.467^{***}	157641.251	56.195^{***}
T x A	3	1428.484	0.038^{ns}	141.536	0.050^{ns}
Error	12	37453.313		2805.241	
R x A	3	44371.875	0.230^{ns}	6957.792	0.700^{ns}
T x R x A	3	2490.719	0.013^{ns}	171.052	0.017^{ns}
Error	12	193334.078		9940.791	

APPENDIX 5.6

ANALYSIS OF VARIANCE OF DRY WEIGHT OF SHOOT AND ROOT (g/pot)

Source of Variation	D.F.	Shoot Dry Weight (g/pot)		Root Dry Weight (g/pot)	
		M.S.	V.R.	M.S.	V.R.
Block	2	0.001	0.017^{ns}	0.0005	0.5^{ns}
Type O.M. (T)	1	0.055	0.917^{ns}	0.002	2.000^{ns}
Error	2	0.06		0.001	
Rate O.M. (R)	1	0.621	23.00^{**}	0.114	19.000^{*}
T x R	1	0.027	1.000^{ns}	0.007	1.167^{ns}
Error	4	0.027		0.006	
Rate Al (A)	3	0.959	26.639^{***}	0.132	18.857^{***}
T x A	3	0.002	0.016^{ns}	0.000	
Error	12	0.036		0.007	
R x A	3	0.006	0.086^{ns}	0.010	1.429^{ns}
T x R x A	3	0.004	0.057^{ns}	0.001	0.143
Error	12	0.070		0.007	

APPENDIX 5.7

ANALYSIS OF VARIANCE OF EXCHANGEABLE ALUMINIUM AND MONOMERIC ALUMINIUM CONCENTRATION IN SOIL AND SOIL SOLUTION

Source of Variation	D.F.	Al (µg/gram)		Monomeric Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	137.386	3.805^{ns}	48.088	1.790^{ns}
Type O.M. (T)	1	1785.104	49.436^{*}	13.771	0.513^{ns}
Error	2	36.109		26.860	
Rate O.M. (R)	1	147816.482	1082.572^{***}	4306.388	916.838^{***}
T x R	1	2136.802	15.649^{*}	13.262	2.824^{ns}
Error	4	136.542		4.697	
Rate Al (A)	3	8195.198	66.079^{***}	3208.340	222.153^{***}
T x A	3	2.860	0.023^{ns}	5.023	0.348^{ns}
Error	12	124.022		14.442	
R x A	3	3109.467	3.817^{*}	1646.796	74.933^{***}
T x R x A	3	101.377	0.124^{ns}	6.517	0.297^{ns}
Error	12	814.741		21.977	

APPENDIX 5.8

ANALYSIS OF VARIANCE OF TOTAL AND ORGANICALLY COMPLEXED ALUMINIUM CONCENTRATION IN SOIL SOLUTION

Source of Variation	D.F.	Total Al (µM)		Organic Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	21.202	1.612^{ns}	6.852	2.088^{ns}
Type O.M. (T)	1	27.907	2.122^{ns}	2.471	0.753^{ns}
Error	2	13.152		3.281	
Rate O.M. (R)	1	30.337	2.583^{ns}	5059.619	1831.205^{***}
T x R	1	103.019	8.772^{*}	42.356	15.330^{*}
Error	4	11.744		2.763	
Rate Al (A)	3	6945.478	396.703^{***}	789.750	48.424^{***}
T x A	3	0.051	0.003^{ns}	5.861	0.359^{ns}
Error	12	17.508		16.309	
R x A	3	541.655	8.709^{**}	306.316	7.193^{**}
T x R x A	3	1.359	0.022^{ns}	6.831	0.160^{ns}
Error	12	62.194		42.584	

APPENDIX 5.9

ANALYSIS OF VARIANCE OF SOIL pH AND IONIC STRENGTH IN SOIL SOLUTION

Source of Variation	D.F.	pH		Ionic Strength	
		M.S.	V.R.	M.S.	V.R.
Block	2	0.081	1.350^{ns}	0.488	1.36^{ns}
Type O.M. (T)	1	0.047	0.780^{ns}	0.594	1.65^{ns}
Error	2	0.060		0.36	
Rate O.M. (R)	1	9.452	18.754^{*}	188.46	77.49^{***}
T x R	1	0.011	0.022^{ns}	2.586	1.063^{ns}
Error	4	0.504		2.432	
Rate Al (A)	3	0.347	6.804^{**}	10.542	26.159^{***}
T x A	3	0.005	0.098^{ns}	0.273	0.677^{ns}
Error	12	0.051		0.403	
R x A	3	0.010	0.010^{ns}	0.293	0.066^{ns}
T x R x A	3	0.002	0.002^{ns}	0.132	0.03^{ns}
Error	12	0.992		4.453	

APPENDIX 5.10

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION

IN SOIL AND SOIL SOLUTION

Source of Variation	D.F.	P in soil (µg/gram)		P in soil solution (µg/gram)	
		M.S.	V.R.	M.S.	V.R.
Block	2	44.507	0.886^{ns}	0.009	0.231^{ns}
Type O.M. (T)	1	1042.163	20.74^{*}	0.859	22.026^{*}
Error	2	50.25		0.039	
Rate O.M. (R)	1	10112.310	124.372^{***}	9.083	189.229^{***}
T x R	1	893.723	10.992^{*}	0.924	19.250^{*}
Error	4	81.307		0.048	
Rate Al (A)	3	3369.747	28.270^{***}	1.981	44.022^{***}
T x A	3	37.307	0.313^{ns}	0.029	0.644^{ns}
Error	12	119.199		0.045	
R x A	3	29.956	0.254^{ns}	0.240	3.077^{ns}
T x R x A	3	3.635	0.031^{ns}	0.012	0.154^{ns}
Error	12	118.143		0.078	

APPENDIX 5.11

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION AND CONTENT IN PLANT

Source of Variation	D.F.	P Concentration (µg/g)		P Content (µg/plant)	
		M.S.	V.R.	M.S.	V.R.
Block	2	19908.53	1.231^{ns}	1288.71	0.999^{ns}
Type O.M. (T)	1	52232.531	3.231^{ns}	7870.207	6.103^{ns}
Error	2	16168.00		1289.50	
Rate O.M. (R)	1	861405.797	100.461^{***}	76999.329	176.155^{***}
T x R	1	46090.688	5.375^{ns}	5927.632	13.561^{*}
Error	4	8574.492		437.112	
Rate Al (A)	3	807227.485	14.408^{***}	96983.467	23.940^{***}
T x A	3	3317.469	0.059^{ns}	175.457	0.043^{ns}
Error	12	56026.182		4051.125	
R x A	3	34444.109	0.606^{ns}	31.601	0.005^{ns}
T x R x A	3	2464.172	0.043^{ns}	156.420	0.026^{ns}
Error	12	56875.672		6112.484	

APPENDIX 5.12

ANALYSIS OF VARIANCE OF DRY WEIGHT OF SHOOT AND ROOT (g/pot)

Source of Variation	D.F.	Shoot Dry Weight (g/pot)		Root Dry Weight (g/pot)	
		M.S.	V.R.	M.S.	V.R.
Block	2	0.015	0.470^{ns}	0.002	1.00^{ns}
Type O.M. (T)	1	0.035	1.061^{ns}	0.008	5.33^{ns}
Error	2	0.033		0.0015	
Rate O.M. (R)	1	1.397	349.250^{***}	0.195	27.857^{**}
T x R	1	0.049	12.250^{*}	0.007	1.000^{ns}
Error	4	0.004		0.007	
Rate Al (A)	3	1.417	37.289^{***}	0.163	20.375^{***}
T x A	3	0.003	0.079^{ns}	0.001	0.125^{ns}
Error	12	0.038		0.008	
R x A	3	0.145	1.933^{ns}	0.007	0.389^{ns}
T x R x A	3	0.001	0.013^{ns}	0.000	
Error	12	0.075		0.018	

APPENDIX 6.1

ANALYSIS OF VARIANCE OF EXCHANGEABLE ALUMINIUM AND MONOMERIC ALUMINIUM CONCENTRATION IN SOIL AND SOIL SOLUTION

Source of Variation	D.F.	Al (µg/gram)		Monomeric Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	166.560	0.359^{ns}	2.612	0.191^{ns}
Type O.M. (T)	1	720.983	1.553^{ns}	0.018	0.001^{ns}
Error	2	464.265		13.673	
Rate O.M. (R)	1	108686.995	291.899^{***}	214.969	34.445^{**}
T x R	1	285.139	0.766^{ns}	1.074	0.172^{ns}
Error	4	372.344		6.241	
Rate P (P)	3	1930.017	5.886^{**}	50.385	6.177^{**}
T x P	3	150.309	0.458^{ns}	0.910	0.112^{ns}
Error	12	327.904		8.157	
R x P	3	851.899	2.432^{ns}	20.656	4.357^{*}
T x R x P	3	149.555	0.427^{ns}	0.289	0.061^{ns}
Error	12	350.355		4.741	

APPENDIX 6.2

ANALYSIS OF VARIANCE OF TOTAL AND ORGANIC ALUMINIUM CONCENTRATION IN SOIL SOLUTION

Source of Variation	D.F.	Total Al (µM)		Organic Al (µM)	
		M.S.	V.R.	M.S.	V.R.
Block	2	35.369	1.593^{ns}	18.796	0.393^{ns}
Type O.M. (T)	1	4.681	0.211^{ns}	5.287	0.108^{ns}
Error	2	22.195		49.070	
Rate O.M. (R)	1	28094.750	138.428^{***}	33224.794	136.563^{***}
T x R	1	302.957	1.493^{ns}	340.108	1.398^{ns}
Error	4	202.956		243.292	
Rate P (P)	3	11748.755	99.835^{***}	13164.992	100.017^{***}
T x P	3	64.197	0.546^{ns}	67.887	0.516^{ns}
Error	12	117.682		131.627	
R x P	3	1408.121	20.388^{***}	1389.355	21.613^{***}
T x R x P	3	35.303	0.511^{ns}	35.696	0.555^{ns}
Error	12	69.065		64.283	

APPENDIX 6.3

ANALYSIS OF VARIANCE OF pH AND IONIC STRENGTH (I.S.) IN SOIL SOLUTION AND pH IN SOIL

Source of Variation	D.F.	pH in soil		pH in soil solution		I.S.in soil solution (meq/100g)	
		M.S.	V.R.	M.S.	V.R.	M.S.	V.R.
Block	2	0.071	8.875^{NS}	0.011	0.091^{NS}	1.277	13.31^{NS}
Type O.M. (T)	1	0.407	50.875^{*}	0.031	0.248^{NS}	15.576	162.25^{**}
Error	2	0.008		0.125		0.096	
Rate O.M. (R)	1	6.453	58.664^{**}	8.102	47.941^{**}	306.803	142.898^{***}
T x R	1	0.472	4.291^{NS}	0.060	0.355^{NS}	15.297	7.125^{NS}
Error	4	0.110		0.169		2.147	
Rate P (P)	3	0.143	2.648^{NS}	2.431	12.095^{***}	1.558	1.125^{NS}
T x P	3	0.002	0.037^{NS}	0.039	0.194^{NS}	0.42	0.303^{NS}
Error	12	0.054		0.201		1.385	
R x P	3	0.005	0.036^{NS}	0.271	0.944^{NS}	4.535	1.372^{NS}
T x R x P	3	0.001	0.007^{NS}	0.046	0.160^{NS}	0.09	0.027^{NS}
Error	12	0.140		0.287		3.305	

APPENDIX 6.4

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION IN SOIL

Source of Variation	D.F.	P in soil (µg/gram)	
		M.S.	V.R.
Block	2	75.965	3.801^{ns}
Type O.M. (T)	1	439.654	22.000^{*}
Error	2	19.984	
Rate O.M. (R)	1	4163.246	29.183^{**}
T x R	1	228.071	1.599^{ns}
Error	4	142.659	
Rate P (P)	3	5123.639	474.016^{***}
T x P	3	5.958	0.551^{ns}
Error	12	10.809	
R x P	3	124.146	1.845^{ns}
T x R x P	3	25.103	0.373^{ns}
Error	12	67.300	

APPENDIX 6.5

ANALYSIS OF VARIANCE OF PHOSPHORUS CONCENTRATION AND CONTENT IN PLANT

Source of Variation	D.F.	P Concentration (µg/g)		P Content (µg/plant)	
		M.S.	V.R.	M.S.	V.R.
Block	2	22386.25	0.301^{ns}	5368.001	3.285^{ns}
Type O.M. (T)	1	274836.656	3.694^{ns}	16647.773	10.189^{ns}
Error	2	74400.000		1633.875	
Rate O.M. (R)	1	2892235.689	27.688^{**}	211715.085	72.280^{**}
T x R	1	123474.563	1.182^{ns}	10444.767	3.566^{ns}
Error	4	104458.539		2929.114	
Rate P (P)	3	16860835.227	201.139^{***}	576517.313	126.500^{***}
T x P	3	19366.375	0.231^{ns}	1631.665	0.358^{ns}
Error	12	83826.820		4557.444	
R x P	3	62872.938	0.356^{ns}	24066.318	4.701^{*}
T x R x P	3	22357.156	0.126^{ns}	1763.721	0.345^{ns}
Error	12	176808.057		5119.276	

APPENDIX 6.6

ANALYSIS OF VARIANCE OF DRY WEIGHT OF SHOOT AND ROOT (g/pot)

Source of Variation	D.F.	Shoot Dry Weight (g/pot)		Root Dry Weight (g/pot)	
		M.S.	V.R.	M.S.	V.R.
Block	2	2.480	4.502^{ns}	0.105	1.77^{ns}
TypeO.M. (T)	1	3.521	6.390^{ns}	0.349	5.915^{ns}
Error	2	0.551		0.059	
Rate O.M. (R)	1	55.041	71.389^{**}	7.293	57.881^{**}
T x R	1	2.001	2.595^{ns}	0.309	2.452^{ns}
Error	4	0.771		0.126	
Rate P (P)	3	301.596	171.556^{***}	45.234	675.134^{***}
T x P	3	0.176	0.100^{ns}	0.113	1.687^{ns}
Error	12	1.758		0.067	
R x P	3	4.439	1.962^{ns}	0.480	1.860^{ns}
T x R x P	3	0.126	0.056^{ns}	0.018	0.070^{ns}
Error	12	2.262		0.258	